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THE GROUND-STATE OF THE Se_2 MOLECULE.

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The diatomic molecules of the lighter elements of the sixth family of the Periodic Table show the peculiarity that contrary to the behaviour of other groups the ground-level is a triplet state. Ordinarily, one should expect that on combination of two atoms, each of which is in a ^3P state, a molecule with $^1\Sigma$ as its ground-level should result and that the possible triplet states are excited ones. It has, however, been established by experiment[1]—and upto a certain extent also theoretically—that in the O_2, S_2 and SO molecules the ground-level is $^3\Sigma$ and that the $^1\Sigma$ level is some way above it.

There is some doubt, whether or not this condition still prevails with the other elements of that group. It is possible that as one proceeds to heavier atoms the $^1\Sigma$ state may come below $^3\Sigma$. Spectroscopical investigations have so far not been able to bring about a decision and it is still unknown, whether the ground-states of Se_2, Te_2, SeO, etc., are $^3\Sigma$ or $^1\Sigma$ states.[1]

So it appeared worthwhile to ascertain the magnetic properties of Se_2 vapour and to bring about a decision in this way. A Weiss-Foëx transmission balance would have been the proper apparatus for that purpose, especially if accurate values for the susceptibility of Se_2 vapour were to be found out. That type of balance was, however, not at our disposal. On the other hand, the actual value of the susceptibility of the vapour is not of particular importance; what is really wanted, is a qualitative experiment to show whether the vapour is paramagnetic or diamagnetic. Furthermore, there is no point in exaggerating the accuracy of the magnetic measurements, because the vapour pressure of Se_2 at various temperatures is not sufficiently well known to justify the employment of a more sensitive apparatus. Therefore, the simplest possible arrangement was decided upon.

A furnace made of a double filament of coiled nichrome wire was placed between the poles of an electro-magnet of about 7000 gauss. In the earlier experiments the pole-pieces of the magnet were cooled with water, but later

on it was found that it really did not matter, because it was possible to insulate the furnace so well with a mixture of asbestos and clay, that even without cooling the field remained unchanged in the degree of accuracy attained.

The sample was hanging inside the furnace and was suspended from an analytical balance with the help of a silica fibre. The selenium was carefully purified, special care was taken to prevent the surface of the grains from being contaminated by a layer of oxides. It was then sealed in a silica tube in the vacuum, the evacuation being driven to a point when the cathode ray discharge practically ceased. Care was also taken to remove any air adsorbed on the walls of the tube, before the sample was introduced.

The method of reading was a null method, the force exerted by the magnet being counterbalanced by the addition of weights. This force, according to the different tubes used, varied between 0·0016 and 0·0038 g.

The temperatures were measured with the help of a pyrometer (thermocouple and millivoltmeter) ; the gauging was checked with the help of various standard temperatures (b.p. of sulphur, m.p. of sodium chloride, etc.).

The measurements on the empty and evacuated tubes showed not the slightest change in the force exerted by the magnet between room temperature and 1100° C. ; the changes in the field, which were due to a slight warming of the pole-pieces and to heating the air between them, were apparently below the sensitivity of the apparatus.

The tubes containing selenium exhibited on heating a considerable reduction of the force exerted by the magnet and thus showed that the selenium vapour formed in them was *paramagnetic*.

A few examples of the measurements taken are as follows :—

TUBE III.

Weight (empty) = 2·3842 g.
Capacity = 1·0429 cm³.
Se inside = 0·0186 g.

Temperature	Magnetic Force
23° C.	— 0·0036 g.
481° C.	— 0·0036 g.
648° C.	— 0·0036 g.
783° C.	— 0·0033 g.
923° C.	— 0·0032 g.
1110° C.	— 0·0030 g.

TUBE IV.

Weight (empty) = 1·4141 g.
Capacity = 0·3910 cm³.
Se inside = 0·0189 g.

Temperature	Magnetic Force
23° C.	— 0·0024 g.
440° C.	— 0·0024 g.
523° C.	— 0·0023 g.
648° C.	— 0·0022 g.
783° C.	— 0·0020 g.
970° C.	— 0·0018 g.
1110° C.	— 0·0016 g.

From these results there is not the least doubt that on heating a considerable quantity of a paramagnetic vapour is created in the tubes. On the other hand, it was not possible to calculate a value for the susceptibility of Se_2 vapour with any semblance of accuracy, because the amount of Se_2 formed in the tubes was quite unknown. The formula of Preuner and Brockmüller[2] for the equilibrium between Se_6 and Se_2 gave by far too low values for the quantity of Se_2 present. On the other hand, there is no reason to suppose that the paramagnetic susceptibility of free Se_2 molecules should in any way be different from that of O_2, particularly in consideration of the fact, that there is an excellent agreement between the theoretical value for a $^3\Sigma$ state and the one measured on oxygen.[3]

Experiments with sulphur made along with those on selenium confirmed qualitatively the results previously obtained by Néel.[4] As to the actual amount of the susceptibility of S_2 calculated by him, the present authors are of opinion that the same holds good as in the case of Se_2 and that in spite of the accuracy of his magnetic measurements the amount of S_2 present in the sulphur vapour is not sufficiently well known to justify any statement as to the numerical value of the susceptibility. The discrepancy found by Néel between his value and the theoretical one is probably due to that cause rather than to a real deviation.

Experiments to ascertain, whether Te_2 vapour is dia- or paramagnetic, are in progress. Here higher temperatures are necessary than for sulphur and selenium, and the furnace employed in those cases was insufficient for tellurium.

The apparatus described proved to be a quick and efficient means of ascertaining the magnetic nature of vapours, particularly in cases, when it is either not necessary or—owing to lack of knowledge as to the vapour pressure—not possible to obtain accurate values of the susceptibility.

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[1] Literature in H. Sponer, *Molekülspektren*, Berlin, 1935, 1.

[2] G. Preuner and J. Brockmüller, *Zs. physik. Chem.*, 1913, **81**, 129.

[3] J. H. Van Vleck, *Electric and Magnetic Susceptibilities*, Oxford, 1932, 266; E. C. Stoner, *Magnetism and Matter*, London, 1934, 340; S. S. Bhatnagar and K. N. Mathur, London, 1935, 172.

[4] L. Néel, *C.R.*, 1932, **194**, 2035.

GENERALISED ACTION-FUNCTIONS IN BORN'S ELECTRO-DYNAMICS.

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1. Introduction.

Infeld has shown[1] that, in the development of Born's field theory, it is possible to choose an infinity of action-functions other than the one originally proposed by Born and Infeld[2] which, for simplicity, might be called Born's action-function. These action-functions of Infeld and the one recently introduced by Hoffmann and Infeld[3] have, in common with Born's action-function, the properties of self-conjugacy, of the existence of simple, algebraic relations between the f_{kl}- and p_{kl}-fields, and giving finite values for the energy for the electrical particle. They, however, differ from the latter in that the condition of the invariance of the action-integral itself is not insisted in them. As I have shown elsewhere[4] Born's function is unique if this condition as well as the condition of self-conjugacy are imposed on the action-function.

Laying aside for the present this condition of invariance of the action-integral, we might say that the action-functions of Infeld and Hoffmann and Infeld give rise to several systems of Born's non-linear electro-dynamics. These action-functions, however, are all confined to the case where the invariant $G = (\vec{B}\,\vec{E})$ is neglected, as also the invariants $Q = (\vec{D}\,\vec{H})$, and $S = (\vec{B}\,\vec{D}) + (\vec{E}\,\vec{H})$. I have considered in this paper the general case where these invariants are not neglected and constructed a two-fold infinity of action-functions all having the same properties as Infeld's action-functions and reducing to them when $G = 0$. This generalisation has also enabled the deduction of close connections with the complex formalism developed by Weiss.[5] In view of the fact however, that the condition of " finite self-energy " has so far been discussed in the case of the point-singularity and

[1] Infeld, *Proc. Camb. Phil. Soc.*, 1936, **32**, 127 ; 1937, **33**, 70—hereinafter referred to as I and II.

[2] Born and Infeld, *Proc. Roy. Soc.*, (A), 1934, **144**, 425.

[3] Hoffmann and Infeld, *Phys. Rev.*, 1937, **51**, 765—hereinafter referred to as III.

[4] B. S. Madhava Rao, *Proc. Ind. Acad. Sci.*, (A), 1936, **3**, 377.

[5] P. Weiss, *Proc. Camb. Phil. Soc.*, 1937, **33**, 79—hereinafter referred to as IV.

the case of ring-singularity in the zero-approximation[6] where, in both cases, the invariant G does not appear, it seems difficult to set up a criterion limiting the choice of these action-functions. Nor is the regularity condition of Hoffmann and Infeld of any use since it is based on the character of a spherically symmetric electro-static solution.

An attempt has been made in this paper to construct an action-function which leads to a full coincidence of the second order terms when the Lagrangian of the field theory is compared with the Lagrangian that arises in the investigations of Euler and Köckel[7] on the phenomenon of scattering of light by light on the basis of Dirac's theory of holes. It is well known that such a coincidence does not exist[8] in the terms containing G^2 when Born's action-function is used. The result that I obtain is that even this condition does not restrict the choice of the action-function there being more than one such function wherefrom a coincidence with the Euler-Köckel Lagrangian could be obtained as well as the good determination of the fine-structure constant possible with the Hoffmann-Infeld action-function.

I have closely followed the method adopted by Infeld in I and II.

2. *Condition of Self-conjugacy.*

We introduce the f_{kl} and p^{kl} (or in the dual form f^{*kl} and p_{kl}^{*}) tensors describing the electromagnetic field, the space-vector notation and also the several invariants in the usual manner,[9] with the modification introduced by Weiss,[10] which leads to a good lot of simplification by avoiding unnecessary numerical factors. The Lorentz frame of reference is used.

$$\left.\begin{aligned} (f_{23}, f_{31}, f_{12}) &= \vec{B}, \quad (f_{14}, f_{24}, f_{34}) = \vec{E} \\ (p_{23}, p_{31}, p_{12}) &= \vec{H}, \quad (p_{14}, p_{24}, p_{34}) = \vec{D} \end{aligned}\right\} \qquad (2,\ 1)$$

$$\left.\begin{aligned} \tfrac{1}{4} f_{kl} f^{kl} &= -\tfrac{1}{4} f^{*kl} f_{kl}^{*} = F, \quad \tfrac{1}{4} f_{kl} f^{*kl} = \tfrac{1}{4} f_{kl}^{*} f^{kl} = G, \\ \tfrac{1}{4} p_{kl}^{*} p^{*kl} &= -\tfrac{1}{4} p_{kl} p^{kl} = P, \quad \tfrac{1}{4} p_{kl}^{*} p^{kl} = \tfrac{1}{4} p_{kl} p^{*kl} = Q, \\ \tfrac{1}{4} f_{kl} p^{kl} &= -\tfrac{1}{4} f^{*kl} p_{kl}^{*} = R, \quad \tfrac{1}{4} f_{kl} p^{*kl} = \tfrac{1}{4} f^{*kl} p_{kl} = S \end{aligned}\right\} \qquad (2,\ 2)$$

$$\left.\begin{aligned} F &= \tfrac{1}{2}(\vec{B}^2 - \vec{E}^2), \quad G = (\vec{B}\,\vec{E}) \\ P &= \tfrac{1}{2}(\vec{D}^2 - \vec{H}^2), \quad Q = (\vec{D}\,\vec{H}) \\ R &= \tfrac{1}{2}\{(\vec{B}\,\vec{H}) - (\vec{D}\,\vec{E})\}, \quad S = \tfrac{1}{2}\{(\vec{B}\,\vec{D}) + (\vec{E}\,\vec{H})\} \end{aligned}\right\} \qquad (2,\ 3)$$

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[6] B. S. Madhava Rao, *Proc. Ind. Acad. Sci.*, (A), 1936, **4**, 355.

[7] Euler and Köckel, *Naturwiss.*, 1935, **23**, 246.

[8] M. Born, *Proc. Ind. Acad. Sci.*, (A), 1935, **2**, 560.

[9] B. S. Madhava Rao, *Proc. Ind. Acad. Sci.*, (A), 1936, **4**, 578, §3—hereafter referred to as V.

[10] IV, foot-note p. 80.

We impose on our action-function T, which we assume to be a function of F, G, P and Q, that it should be self-conjugate. This means that the set of equations

$$p^{kl} = \frac{\partial T}{\partial f_{kl}} \Bigg\} \qquad (2, 4)$$

$$f^{*kl} = \frac{\partial T}{\partial p_{kl}^{*}} \Bigg\} \qquad (2, 5)$$

should be self-consistent, *i.e.*, that (2, 5) is a consequence of (2, 4), or *vice versa*. We can rewrite (2, 4) and (2, 5) in the form

$$p^{kl} = T_F f^{kl} + T_G f^{*kl} \Big\} \qquad (2, 6)$$

$$f^{*kl} = T_P p^{*kl} + T_Q p^{kl} \Big\} \qquad (2, 7)$$

where T_F, T_P, T_G, T_Q denote the derivatives with respect to F, P, G, Q respectively. We shall now find the restriction to be imposed on T to ensure the consistency of (2, 6) and (2, 7). We multiply (2, 6) respectively by $\frac{1}{4}f_{kl}$, $\frac{1}{4}f_{kl}^{*}$, $\frac{1}{4}p_{kl}$, $\frac{1}{4}p_{kl}^{*}$ and sum up; similarly (2, 7) respectively by $\frac{1}{4}p_{kl}^{*}$, $\frac{1}{4}p_{kl}$, $\frac{1}{4}f_{kl}^{*}$, $\frac{1}{4}f_{kl}$ and sum up. We get[11] after suitably grouping the terms

$$R = FT_F + GT_G \Big\} \qquad (2, 8)$$

$$-R = PT_P + QT_Q \Big\} \qquad (2, 9)$$

$$S = GT_F - FT_G \Big\} \qquad (2, 10)$$

$$S = QT_P - PT_Q \Big\} \qquad (2, 11)$$

$$-P = RT_F + ST_G \Big\} \qquad (2, 12)$$

$$F = RT_P - ST_Q \Big\} \qquad (2, 13)$$

$$Q = ST_F - RT_G \Big\} \qquad (2, 14)$$

$$G = ST_P + RT_Q \Big\} \qquad (2, 15)$$

The equations (2, 9), (2, 11), (2, 13) and (2, 15) must follow as consequences from (2, 8), (2, 10), (2, 12) and (2, 14) respectively.

Before proceeding to reduce the above number of eight equations we will directly obtain two conditions which follow from the self-consistency of (2, 6) and (2, 7). Taking the dual of (2, 6) we get

$$p^{*kl} = T_F f^{*kl} + T_G f^{**kl} = T_F f^{*kl} - T_G f^{kl};$$

Substituting this value of p^{*kl} and the value of p^{kl} from (2, 6) in (2, 7) we should get an identical equation, *i.e.*,

$$f^{*kl} = T_P (T_F f^{*kl} - T_G f^{kl}) + T_Q(T_F f^{kl} + T_G f^{*kl})$$

identically. This leads to the consistency conditions

$$T_F T_P + T_G T_Q = 1 \qquad (2, 16)$$

$$T_F T_Q - T_P T_G = 0 \qquad (2, 17)$$

---

[11] As in V, p. 579, where we replace both L and H by T and introduce the necessary numerical factors to correspond to Weiss's notation.

It is now easy to see with the aid of (2, 16) and (2, 17) that the equations (2, 12)—(2, 15) are consequences of (2, 8)—(2, 11). Hence the eight equations (2, 8)—(2, 15) can be reduced to the six equations (2, 8)—(2, 11) and (2, 16)—(2, 17).

In essence we have replaced the four equations (2, 12)—(2, 15) by the two equations (2, 16) and (2, 17). We can now find two other equations equivalent to the latter. From (2, 12)—(2, 15) and using (2, 16)—(2, 17) it is very easy to deduce the following two relations between the invariants, *viz.*,

$$S^2 - R^2 = FP + GQ \qquad (2, 18)$$

$$2RS = FQ - PG \qquad (2, 19)$$

Further using (2, 8)—(2, 15) and (2, 18)—(2, 19) it is easy to deduce (2, 16) and (2, 17). Thus the original system of eight equations can be reduced to the six equations (2, 8)—(2, 11) and (2, 18)—(2, 19). These last two equations are relations between the invariants, F, G, Q, R and S which hold as a consequence of the condition of self-conjugacy. But they are exactly the same as those obtained by Weiss[12] by expressing the symmetry of the energy-impulse tensor. Thus the *relation between the invariants imposed by self-conjugacy is the same as that obtained by making the energy-impulse tensor symmetrical.*

Coming now to the conditions (2, 8)—(2, 11) we can rewrite them in the forms

$$FT_F + GT_G + PT_P + QT_Q = 0 \qquad (2, 20)$$

$$GT_F - FT_G - QT_P + PT_Q = 0 \qquad (2, 21)$$

and

$$FT_F + GT_G - PT_P - QT_Q = 2R \qquad (2, 22)$$

$$GT_F - FT_G + QT_P - PT_Q = 2S \qquad (2, 23)$$

(2, 20)—(2, 21) form a system of simultaneous partial differential equations for T in the homogeneous form—in particular (2, 20) shows that T must be a homogeneous function of degree zero in F, G, P, Q. If we, therefore, choose T so as to satisfy these relations (2, 20)—(2, 21) we will have reduced our original eight equations to four only in consonance with the consistency condition. The equations (2, 20)—(2, 21) would then be identically satisfied, (2, 18)—(2, 19) or (2, 16)—(2, 17) would give the relations between the invariants, and (2, 22)—(2, 23) would give P, Q, R, S as functions of F and G.

[12] See IV, p. 85, equation (4, 5).

3. Solution of the System of Partial Differential Equations.

In the usual notation of the theory of partial differential equations we can write (2, 20)—(2, 21) as

$$F_1 \equiv x_1 p_1 + x_2 p_2 + x_3 p_3 + x_4 p_4 = 0 \quad (3, 1)$$

$$F_2 \equiv x_2 p_1 - x_1 p_2 - x_4 p_3 + x_3 p_4 = 0 \quad (3, 2)$$

and proceed to find out the most general functional form of the solution common to (3, 1)—(3, 2).

It is easy to verify that the Poisson bracket $(F_1, F_2) = 0$, so that the equations form a complete Jacobian system as they are. The most general solution of (3, 1) is any arbitrary function of $(x_2/x_1, x_3/x_1, x_4/x_1)$. Adopting the usual method we introduce new variables given by

$$x_1 = x_1,\ u = x_2/x_1,\ v = x_3/x_1,\ w = x_4/x_1.$$

With these substitutions, equation (3, 1), *i.e.*,

$$x_1 \frac{\partial f}{\partial x_1} + x_2 \frac{\partial f}{\partial x_2} + x_3 \frac{\partial f}{\partial x_3} + x_4 \frac{\partial f}{\partial x_4} = 0$$

reduces to $\dfrac{\partial f}{\partial x_1} = 0$; and the second equation (3, 2), *i.e.*,

$$x_2 \frac{\partial f}{\partial x_1} - x_1 \frac{\partial f}{\partial x_2} - x_4 \frac{\partial f}{\partial x_3} + x_3 \frac{\partial f}{\partial x_4} = 0 \text{ reduces to}$$

$$x_2\left(\frac{\partial f}{\partial x_1} - \frac{u}{x_1} f_u - \frac{v}{x_1} f_v - \frac{w}{x_1} f_w\right) - x_1\left(\frac{1}{x_1} f_u\right) - x_4\left(\frac{1}{x_1} f_v\right) + x_3\left(\frac{1}{x_1} f_w\right) = 0,$$

i.e., $$-u^2 f_u - uv f_v - uw f_w - f_u - w f_v + v f_w = 0$$

or $$f_u (1 + u^2) + f_v (uv + w) + f_w (uw - v) = 0 \quad (3, 3)$$

The Lagrangian subsidiary equations of (3, 3) are

$$\frac{du}{1+u^2} = \frac{dv}{uv+w} = \frac{dw}{uw - v} \quad (3, 4)$$

and we need only find two independent integrals of (3, 4).

From (3, 4) we can immediately deduce the relations

$$\frac{udu}{1+u^2} = \frac{vdv + wdw}{v^2+w^2}, \text{ and}$$

$$\frac{du}{1+u^2} = \frac{wdv - vdw}{v^2+w^2}.$$

These lead to the two integrals

$$\log (1 + u^2) = \log (v^2 + w^2) + \text{const.},$$

and $\tan^{-1} u - \tan^{-1}\left(\dfrac{v}{w}\right) = \text{const.}$, respectively

or, $$\frac{1+u^2}{v^2+w^2} = \text{const., and } \frac{wu - v}{uv+w} = \text{const.}$$

For reasons to be immediately given, we write,

$$\epsilon = \sqrt{\frac{1+u^2}{v^2+w^2}}; \quad \epsilon' = \frac{uv+w}{wu-v} \left(\text{instead of } \frac{wu-v}{uv+w}\right)$$

or, introducing the invariants F, G, P, Q

$$\epsilon = \sqrt{\frac{F^2+G^2}{P^2+Q^2}}; \quad \epsilon' = \frac{FQ+PG}{FP-GQ} \qquad (3, 5)$$

The most general form of the solution common to (3, 1), (3, 2) is any arbitrary function T (ϵ, ϵ') of ϵ and ϵ'. If T be chosen in this form equations (2, 20)—(2, 21) are identically satisfied.

The reason for choosing ϵ and ϵ' in the forms given by (3, 5) is that we want to have these quantities reduce themselves to the corresponding ones when we go over to Infeld's case where G and Q are neglected. If $G = Q = 0$ then $\epsilon' = 0$, and ϵ reduces to $\pm$ (F/P). We therefore further postulate that the negative sign is to be taken in order that our value of ϵ should be the square of the corresponding ϵ used in Infeld's investigations. We may also observe here that in the limiting Maxwellian case where $G = Q$ and $F = -P$, we have $\epsilon = 1$ and $\epsilon' = 0$.

Thus our generalisation has introduced the additional parameter ϵ' and gives rise to a two-fold infinity of action-functions satisfying the condition of self-conjugacy.

4. T as the Sum of Lagrangian and Hamiltonian.

We will show that, in our general case, if (2, 4)—(2, 5) are satisfied the action-function T can be represented as the sum of a Lagrangian and a Hamiltonian

$$\text{Let} \quad L(F, G) = \tfrac{1}{2}T + R \qquad (4, 1)$$
$$H(P, Q) = \tfrac{1}{2}T - R \qquad (4, 2)$$

where we have put the numerical factor $\frac{1}{2}$ on the right-hand side for T in consonance with the notation of Weiss. From (4, 1)

$$2\,dL = T_F dF + T_G dG + T_P dP + T_Q\, dQ + 2\,dR.$$

From the relations (2, 18)—(2, 19)

$$2\,S dS - 2R dR = F dP + P dF + G dQ + Q dG,$$
$$2\,S dR + 2\,R dS = F dQ + Q dF - G dP - P dG.$$

Eliminating dS from the above equations,

$$2\,dR\,(R^2+S^2) = dF\,(QS-PR) - dG\,(PS+QR) - dP\,(GS+FR) + dQ\,(FS-RG). \qquad (4, 3)$$

We can simplify (4, 3) by obtaining the expressions for the derivatives of T in terms of the invariants. Directly solving (2, 8)—(2, 11) for these

derivatives we obtain,

$$\left.\begin{aligned} T_F &= \frac{FR+GS}{F^2+G^2}\,; \quad T_G = \frac{GR-FS}{F^2+G^2} \\ T_P &= \frac{QS-PR}{P^2+Q^2}\,; \quad T_Q = -\frac{QR+PS}{P^2+Q^2} \end{aligned}\right\} \tag{4, 4}$$

Also from (2, 16) – (2, 17), and (2, 20) – (2, 21)

$$\frac{T_P}{T_F} = \frac{T_Q}{T_G} = \left(\frac{F^2+G^2}{P^2+Q^2}\right)^{\frac{1}{2}} = \epsilon. \tag{4, 5}$$

From (2, 18) – (2, 19) by squaring and adding

$$R^2 + S^2 = \sqrt{(F^2+G^2)(P^2+Q^2)}. \tag{4, 6}$$

Now using (4, 4), (4, 6) and (4, 5) successively we can reduce (4, 3) to

$$2dR = T_F\,dF + T_G\,dG - T_P\,dP - T_Q\,dQ$$

and

$$2\,dL = 2\,T_F\,dF + 2\,T_G\,dG$$

i.e.,

$$\frac{\partial L}{\partial F} = \frac{\partial T}{\partial F}, \text{ and } \frac{\partial L}{\partial G} = \frac{\partial T}{\partial G}$$

i.e., L is the Lagrangian. Analogously we can show that H is the Hamiltonian.

5. *Expressions for the Derivatives of T.*

In (4, 4) above, we have obtained expressions for the derivatives of T in terms of all the six invariants, but since we assume T to be a function of only F, G, P, Q we need expressions for the derivatives which do not involve R and S. This is easily done by finding R and S from (2, 18) and (4, 6) and substituting in (4, 4). A simpler way is to use the equations (2, 12) – (2, 15). From these equations and using the consistency conditions (2, 16) – (2, 17) we get

$$\begin{aligned} FP - GQ &= -(R^2+S^2)(T_F T_P - T_G T_Q) \\ &= (R^2+S^2)(1 - 2\epsilon T_F^2), \text{ using (2, 16) and (4, 5)} \end{aligned}$$

and hence, using (4, 6) and (4, 5)

$$2T_F^2 = \sqrt{\frac{P^2+Q^2}{F^2+G^2}} - \frac{FP-GQ}{F^2+G^2} \tag{5, 1}$$

Similarly

$$2T_G^2 = \sqrt{\frac{P^2+Q^2}{F^2+G^2}} + \frac{FP-GQ}{F^2+G^2} \tag{5, 2}$$

In an entirely analogous manner we get

$$2T_P^2 = \sqrt{\frac{F^2+G^2}{P^2+Q^2}} - \frac{FP-GQ}{P^2+Q^2} \tag{5, 3}$$

$$2T_Q^2 = \sqrt{\frac{F^2+G^2}{P^2+Q^2}} + \frac{FP-GQ}{P^2+Q^2} \tag{5, 4}$$

(5, 3) and (5, 4) follow from (5, 1) and (5, 2) by interchanging F and G with P and Q, and thus determine P and Q as the same functions of F and G and conversely, guaranteeing in this way the self-consistency of (2, 4) and (2, 5).

The equations (5, 1)—(5, 4) express the derivatives T_F, T_G, T_P, T_Q in terms of F, G, P and Q. Since the action-functions we are considering can be taken as arbitrary functions of ϵ and ϵ', we must be able to obtain T_ϵ and $T_{\epsilon'}$, in terms of the invariants, in order that we might get for every special system of electrodynamics particular relations connecting F, G, P, Q. We proceed to determine these expressions for T_ϵ and $T_{\epsilon'}$.

We can express T_F and T_G in terms of T_ϵ and $T_{\epsilon'}$ in the form

$$\left.\begin{aligned} T_F &= T_\epsilon \cdot \epsilon_F + T_{\epsilon'} \cdot \epsilon'_F \\ T_G &= T_\epsilon \cdot \epsilon_G + T_{\epsilon''} \cdot \epsilon'_G \end{aligned}\right\}$$

where ϵ_F, for example, stands for $\partial\epsilon/\partial F$. Solving these for T_ϵ and $T_{\epsilon'}$,

$$\left.\begin{aligned} T_\epsilon\ (\epsilon_F\epsilon'_G - \epsilon_G\epsilon'_F) &= \epsilon'_G T_F - \epsilon'_F T_G \\ -\ T_{\epsilon'}\ (\epsilon_F\epsilon'_G - \epsilon_G\epsilon'_F) &= \epsilon_G T_F - \epsilon_F T_G \end{aligned}\right\}.$$

From (3, 5),

$$\left.\begin{aligned} \epsilon_F &= \frac{1}{\epsilon}\cdot\frac{F}{P^2+Q^2}; \quad \epsilon'_F = -\frac{G(P^2+Q^2)}{(FP-GQ)^2} \\ \epsilon_G &= \frac{1}{\epsilon}\cdot\frac{G}{P^2+Q^2}; \quad \epsilon'_G = \frac{F(P^2+Q^2)}{(FP-GQ)^2} \end{aligned}\right\}$$

Substituting these in the above, and simplifying, we get

$$\left.\begin{aligned} \epsilon' T_\epsilon &= FT_F + GT_G \\ -(1+\epsilon'^2)\ T_{\epsilon'} &= GT_F - FT_G \end{aligned}\right\}$$

Using (2, 8) and (2, 10) these can be simplified to the important equations

$$\left.\begin{aligned} \epsilon' T_\epsilon &= R \\ (1+\epsilon'^2)\ T_{\epsilon'} &= -S \end{aligned}\right\} \qquad \begin{matrix}(5,5)\\(5,6)\end{matrix}$$

From these equations it can be seen that it is the derivatives T_ϵ and $T_{\epsilon'}$ that are relevant for the connection between F, G and P, Q, since we can assume in virtue of Weiss' conditions (2, 18) — (2, 19) that R and S are functions of the remaining invariants. This last procedure of finding R and S as functions of F, G, P, Q involves rather complicated square-root expressions and does not appear suitable for particular cases. We shall now find a slightly different method of procedure by a change of the parameters ϵ, ϵ'.

6. *Introduction of New Parameters.*

We can simplify considerations to a great extent by introducing two new functions λ and μ of the invariants defined by

$$\left.\begin{aligned} \epsilon &= e^\lambda, \quad \text{or } \lambda = \log\epsilon \\ \epsilon' &= \tan\mu, \quad \mu = \tan^{-1}\epsilon' \end{aligned}\right\} \qquad \begin{matrix}(6,1)\\(6,2)\end{matrix}$$

and consider the action-function T as any arbitrary function of λ and μ.

$$\left.\begin{aligned} T_\lambda = T_\epsilon \cdot \frac{\partial \epsilon}{\partial \lambda} &= \epsilon' T_\epsilon \\ T_\mu = T_{\epsilon'} \cdot \frac{\partial \epsilon'}{\partial \mu} &= (1 + \epsilon'^2)\, T_{\epsilon'} \end{aligned}\right\}$$

Hence (5, 5)—(5, 6) reduce to the very simple and striking forms

$$\left.\begin{aligned} T_\lambda &= \quad R \\ T_\mu &= -S \end{aligned}\right\}. \qquad \begin{matrix} (6, 3) \\ (6, 4) \end{matrix}$$

We can also express (5, 1) and (5, 2) in terms of these new parameters λ and μ. Calculating the value of $(FP - GQ)/(F^2 + G^2)$ in terms of ϵ and ϵ', we readily find

$$\left(\frac{FP - GQ}{F^2 + G^2}\right)^2 = \frac{1}{\epsilon^2(1 + \epsilon'^2)}$$

so that

$$\frac{FP - GQ}{F^2 + G^2} = \pm \frac{1}{\epsilon \sqrt{1 + \epsilon'^2}}.$$

The choice of the + or − sign is decided by going to the limiting case of Infeld's action-functions. In this case the left-hand side reduces to P/F, and since we have already assumed (§3) that in this limiting case ($\epsilon' = 0$) we should take our ϵ as $(-F/P)$ we choose the negative sign and write

$$\frac{FP - GQ}{F^2 + G^2} = -\frac{1}{\epsilon \sqrt{1 + \epsilon'^2}} \qquad (6, 5)$$

Hence (5, 1)—(5, 2) reduce to

$$\left.\begin{aligned} 2T_F^2 &= \frac{1}{\epsilon} + \frac{1}{\epsilon \sqrt{1 + \epsilon'^2}} \\ 2T_G^2 &= \frac{1}{\epsilon} - \frac{1}{\epsilon \sqrt{1 + \epsilon'^2}} \end{aligned}\right\}$$

or, with the substitutions (6, 1) — (6, 2) to

$$\left.\begin{aligned} 2T_F^2 &= 2e^{-\lambda} \cos^2 \tfrac{1}{2}\mu \\ 2T_G^2 &= 2e^{-\lambda} \sin^2 \tfrac{1}{2}\mu \end{aligned}\right\}$$

or

$$\left.\begin{aligned} T_F &= e^{-\lambda/2} \cos \tfrac{1}{2}\mu \\ T_G &= e^{-\lambda/2} \sin \tfrac{1}{2}\mu \end{aligned}\right\} \qquad \begin{matrix} (6, 6) \\ (6, 7) \end{matrix}$$

Making use of (4, 5)

$$\left.\begin{aligned} T_P &= e^{\lambda/2} \cos \tfrac{1}{2}\mu \\ T_Q &= e^{\lambda/2} \sin \tfrac{1}{2}\mu \end{aligned}\right\} \qquad \begin{matrix} (6, 6a) \\ (6, 7a) \end{matrix}$$

Substituting (6, 6)—(6, 7) and (6, 3)—(6, 4) in (2, 12)—(2, 15) we get

$$\left.\begin{aligned} -P &= e^{-\lambda/2} (T_\lambda \cos \tfrac{1}{2}\mu - T_\mu \sin \tfrac{1}{2}\mu) \\ F &= e^{\lambda/2} (T_\lambda \cos \tfrac{1}{2}\mu + T_\mu \sin \tfrac{1}{2}\mu) \end{aligned}\right\} \qquad (6, 8)$$

and,

$$\left.\begin{aligned} Q &= -\epsilon^{-\lambda/2}\,(T_\mu \cos \tfrac{1}{2}\mu + T_\lambda \sin \tfrac{1}{2}\mu) \\ G &= -\epsilon^{\lambda/2}\,(T_\mu \cos \tfrac{1}{2}\mu - T_\lambda \sin \tfrac{1}{2}\mu) \end{aligned}\right\} \qquad (6, 9)$$

Eliminating λ and μ between the four equations (6, 8)—(6, 9) we get two relations between the invariants F, G, P, Q.

7. Relations with the Complex Formalism of Weiss.

The parameters λ and μ are very closely connected with the complex invariants

$$\phi = F + iG$$
$$\psi = P - iQ$$

introduced by Weiss.[13] Forming the complex parameter $\lambda + i\mu$,

$$\begin{aligned} \lambda + i\mu &= \log \epsilon + i \tan^{-1} \epsilon' \\ &= \log \sqrt{F^2 + G^2} - \log \sqrt{P^2 + Q^2} + i \tan^{-1} \left\{\frac{(G/F) + (Q/P)}{1 - (G/F)(Q/P)}\right\}. \\ &= \left\{\log \sqrt{F^2 + G^2} + i \tan^{-2}\left(\frac{G}{F}\right)\right\} - \left\{\log \sqrt{P^2 + Q^2} - i \tan^{-1}\left(\frac{P}{Q}\right)\right\} \\ &= \log (F + iG) - \log (P - iQ) \\ &= \log \left(\frac{\phi}{\psi}\right) \end{aligned}$$

$$i.e., \quad \frac{\phi}{\psi} = e^{\lambda + i\mu}. \qquad (7, 1)$$

From the above equation we see that $\lambda + i\mu$ is an analytic function of both the complex variables ϕ and ψ; hence the Cauchy-Riemann conditions give

$$\left.\begin{aligned} \frac{\partial\lambda}{\partial F} &= \frac{\partial\mu}{\partial G}\,; \frac{\partial\lambda}{\partial G} = -\frac{\partial\mu}{\partial F} \\ \frac{\partial\lambda}{\partial P} &= -\frac{\partial\mu}{\partial Q}\,; \frac{\partial\lambda}{\partial Q} = \frac{\partial\mu}{\partial P} \end{aligned}\right\} \qquad (7, 2)$$

Differentiating (6, 6) and (6, 7) respectively with respect to F and G,

$$\left.\begin{aligned} \frac{\partial^2 T}{\partial F^2} &= -\tfrac{1}{2}T_F \frac{\partial\lambda}{\partial F} - \tfrac{1}{2}T_G \frac{\partial\mu}{\partial F} \\ \frac{\partial^2 T}{\partial G^2} &= -\tfrac{1}{2}T_G \frac{\partial\lambda}{\partial G} + \tfrac{1}{2}T_F \frac{\partial\mu}{\partial G} \end{aligned}\right\}$$

Adding these equations, and using (7, 2), we get the Laplacian equation

$$\left.\begin{aligned} \frac{\partial^2 T}{\partial F^2} + \frac{\partial^2 T}{\partial G^2} &= 0 \\ \text{Similarly,} \quad \frac{\partial^2 T}{\partial P^2} + \frac{\partial^2 T}{\partial Q^2} &= 0 \end{aligned}\right\} \qquad (7, 3)$$

[13] IV, p. 86, equations (5, 7), (5, 8).

These conditions reduce to the Laplacian equations given by Weiss for L and H [see IV, p. 88, eq. (6, 3)] if we observe that, in accordance with our results in § 4.

$$T = L(F, G) + H(P, Q).$$

8. The Maxwellian Case.

This corresponds to $\epsilon = 1$, $\epsilon' = 0$, $\lambda = 0$, $\mu = 0$.

Also we have $F = -P = R$, and $G = Q = S$. From (6, 6) – (6, 7)

$$T_F = T_P = 1, \text{ and } T_G = T_Q = 0$$

Hence, $T = F + P = 0$.

9. Born's Action-Function.

The action-function $T(\lambda, \mu)$ corresponding to Born's case can be found by using the fact that one of the relations between invariants in this case is $G = Q$. Hence from (2, 14) – (2, 5)

$$S \cdot T_F - R T_G = S T_P + R T_Q$$

i.e., $$\frac{R}{S} = \frac{1-\epsilon}{1+\epsilon} \cdot \frac{T_F}{T_G}, \quad \text{using (4, 5)}$$

$$= -\tanh \tfrac{1}{2}\lambda \cos \tfrac{1}{2}\mu, \text{ using (6, 6)} - \text{(6, 7) and (6, 1)} - \text{(6, 2)}.$$

i.e., $$\frac{T_\lambda}{T_\mu} = \tanh \tfrac{1}{2}\lambda \cot \tfrac{1}{2}\mu \qquad (9, 1)$$

Solving this partial differential equation we easily derive

$$T = \frac{\cosh \tfrac{1}{2}\lambda}{\cos \tfrac{1}{2}\mu}$$

as the simplest function satisfying (9, 1). We therefore write Born's action-function in the form

$$T = \frac{2 \cosh \tfrac{1}{2}\lambda}{\cos \tfrac{1}{2}\mu} - 2 \qquad (9, 2)$$

so that in the limiting case $\mu = 0$, this might reduce to Infeld's form.[14]

$$\left.\begin{aligned} \text{Also } R &= T_\lambda = \sinh \tfrac{1}{2}\lambda / \cos \tfrac{1}{2}\mu \\ -S &= T_\mu = (\cosh \tfrac{1}{2}\lambda \sin \tfrac{1}{2}\mu)/\cos^2 \tfrac{1}{2}\mu \end{aligned}\right\}$$

Substituting these values in (6, 8) – (6, 9), we get

$$\left.\begin{aligned} P &= \frac{e^{-\lambda} - \cos \mu}{1 + \cos \mu} \\ F &= \frac{e^{\lambda} - \cos \mu}{1 + \cos \mu} \end{aligned}\right\} \qquad (9, 3)$$

$$G = Q = -\tan \tfrac{1}{2}\mu \qquad (9, 4)$$

[14] II, p. 73, equation (4, 1).

From the above equations we can easily deduce

$$\left.\begin{aligned} e^{\lambda} &= \frac{1+2F-G^2}{1+G^2} \\ \text{and} \quad e^{-\lambda} &= \frac{1+2P-Q^2}{1+Q^2} \end{aligned}\right\} \qquad (9, 3a)$$

so that $$\frac{1+2F-G^2}{1+G^2} = \frac{1+Q^2}{1+2P-Q^2} \qquad (9, 5)$$

which, besides $G = Q$, is the other relation between the invariants in Born's " new field theory ".[15]

A much simpler method of deducing (9, 5) is from (9, 4) itself, for

$$\tan \mu = \frac{2 \tan \tfrac{1}{2}\mu}{1-\tan^2 \tfrac{1}{2}\mu} = \frac{2G}{1-G^2}$$

and, $$\tan \mu = \epsilon' = \frac{FQ+PG}{FP-GQ} = \frac{G(F+P)}{FP-G^2}, \quad \text{since } G = Q$$

$$\therefore \quad \frac{2G}{1-G^2} = \frac{G(F+P)}{FP-G^2}$$

or, $$(F+P)(1-G^2) = 2(FP-G^2)$$

which is only a simplified form of (9, 5).

From the form (9, 2) for Born's action-function we can immediately find the form of the Lagrangian. From (4, 1)

$$L = \tfrac{1}{2}T + R = \tfrac{1}{2}T + T_{\lambda}$$

$$= \frac{\cosh \tfrac{1}{2}\lambda}{\cos \tfrac{1}{2}\mu} - 1 + \frac{\sinh \tfrac{1}{2}\lambda}{\cos \tfrac{1}{2}\mu} = \frac{e^{\lambda/2}}{\cos \tfrac{1}{2}\mu} - 1$$

From (9, 3*a*) and (9, 4) this reduces to

$$L = \sqrt{1+2F-G^2} - 1$$

which is the standard form of Born's Lagrangian.

An alternative form for T can also be obtained in terms of the complex invariants ϕ and ψ of Weiss.

$$\phi = F + iG, \quad \psi = P - iQ$$

and using (9, 3) – (9, 4)

$$\phi(1+\cos \mu) = e^{\lambda} - e^{i\mu}$$
$$\psi(1+\cos \mu) = e^{-\lambda} - e^{-i\mu}$$

Hence $\cos^2 \tfrac{1}{2}\mu\,(\phi+\psi) = \cosh \lambda - \cos \mu$, by addition

i.e., $1 + \cosh \lambda = \cos^2 \tfrac{1}{2}\mu\,(\phi+\psi+2)$

i.e., $$2\phi + 2\psi + 4 = \frac{4 \cosh^2 \tfrac{1}{2}\lambda}{\cos^2 \tfrac{1}{2}\mu}$$

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[15] See for *e.g.* V, p. 576, eqn. (8).

and (9, 2) can be written as

$$T = \sqrt{2\phi + 2\psi + 4} - 2 \qquad (9, 6)$$

From (9, 6) it easily follows that T = Lagrangian + Hamiltonian. In fact, $2\phi + 2\psi + 4 = 2F + 2P + 4$, since G = Q in Born's case and from a known identity[16]

$$\sqrt{2F + 2P + 4} = L + H + 2.$$

The form (9, 6) is more general than the one given by Weiss[17] which holds when the invariant G is neglected. The complex Lagrangian and Hamiltonian given by him for this case are respectively $(1 + 2\phi)^{\frac{1}{2}} - 1$, and $(1 + 2\psi)^{\frac{1}{2}} - 1$ and in this case only we have

$$-2 + \sqrt{1 + 2\phi} + \sqrt{1 + 2\psi} = \sqrt{2\phi + 2\psi + 4} - 2 \qquad (9, 7)$$

in virtue of the relation

$$\phi + 2\phi\psi + \psi = 0.$$

While the left-hand side of (9, 7) is not Born's action-function in the general case where G is not ignored, we have shown that the right-hand side is so.

10. Other Functions.

The one parameter group of action-functions given by Infeld, and the one by Hoffmann and Infeld are given in our notation by

$$T = A \cosh \frac{\lambda}{2} + B \sinh \frac{\lambda}{2} + C\lambda + D \qquad (10, 1)$$

and following the analogy of Born's action-function we can use $\cos \frac{1}{2}\mu$ or $(1/\cos \frac{1}{2}\mu)$ which tend to unity with $\mu = 0$ as a sort of guage-factor to generalise (10, 1). It appears however that there is no criterion which leads to such a kind of generalisation.

In analogy with (9, 2) we can consider

$$T = \frac{e^{\lambda/2}}{\cos \frac{1}{2}\mu} - \tfrac{1}{2}\lambda - 1 \qquad (10, 2)$$

as a sort of generalisation of the Hoffmann-Infeld action-function. We shall use (10, 2) to obtain the corresponding Lagrangian, develop it in power series in F and G and compare it with the Lagrangian set up by Euler and Köckel as a correction to Maxwell's theory on the basis of the phenomenon of scattering of light by light according to Dirac's theory of holes. The reason for this investigation is that with the Hoffmann-Infeld action-function (with G = 0) it is possible to make[18] a much better estimate of the

[16] V, p. 580, eqn. (2, 3).

[17] IV, p. 91, eqn. (8, 5).

[18] This has actually not been done with the Hoffmann-Infeld action-function, but with Infeld's action-function $T = e^{-\lambda/2} + \frac{1}{2}\lambda - 1$ where $L = \frac{1}{2}\log(1 + F)$. It can however be shown that we get the same estimate $1/\alpha \simeq 130$ with the action-function $T = e^{-\lambda/2} - \log\lambda - 1$ where $H = \frac{1}{2}\log(1 + P)$.

fine-structure constant than with Born's action-function. In the latter case there is no correspondence (as mentioned in the Introduction) in the terms containing G^2 in the power series expansion. We shall try to find if this correspondence as well as the better estimate for the fine-structure constant could be secured from (10, 2).

The derivatives T_λ and T_μ are given from (10, 2) in the form

$$\left.\begin{aligned} T_\lambda &= \frac{e^{\lambda/2}}{2\cos\frac{1}{2}\mu} - \frac{1}{2} \\ T_\mu &= \frac{e^{\lambda/2}\sin\frac{1}{2}\mu}{2\cos^2\frac{1}{2}\mu} \end{aligned}\right\} \qquad (10, 3)$$

Also $T_\lambda = R$ gives

$$e^{\lambda/2} = (1 + 2R)\cos\tfrac{1}{2}\mu \qquad (10, 4)$$

From (6, 8) and (6, 9)—(using (10, 3) and (10, 4)

$$\left.\begin{aligned} 2F &= (1 + 2R)^2 - (1 + 2R)\cos^2\tfrac{1}{2}\mu \\ 2G &= -(1 + 2R)\sin\tfrac{1}{2}\mu\cos\tfrac{1}{2}\mu \end{aligned}\right\}, \qquad (10, 5)$$

Since our idea is to obtain the power-series expansion of the Lagrangian obtained from (10, 2) upto the second power in F and G, we assume[19]

$$\left.\begin{aligned} R &= a_0F + a_1F^2 + a_2G^2 \\ \text{and} \quad \cos\tfrac{1}{2}\mu &= 1 + b_0F + b_1F^2 + b_2G^2 \end{aligned}\right\} \qquad (10, 6)$$

since $R \to 0$ as F and $G \to 0$, while $\cos\frac{1}{2}\mu \to 1$. Substituting (10, 6) in (10, 5) and equating coefficients of like powers after neglecting terms of order higher than two, we get,

$$a_0 = 1,\ a_1 = -2,\ a_2 = -2$$
$$b_0 = b_1 = 0,\ b_2 = -2$$

i.e.,

$$\left.\begin{aligned} R &= F - 2F^2 - 2G^2 \\ \cos\tfrac{1}{2}\mu &= 1 - 2G^2 \end{aligned}\right\} \qquad (10, 6a)$$

The Lagrangian L corresponding to (10, 2) is given by

$$\begin{aligned} L &= \tfrac{1}{2}T + R \\ &= 2R - \tfrac{1}{4}\lambda, \text{ using (10, 4)} \end{aligned} \qquad (10, 7)$$

Again from (10, 4) the power-series expansion for λ, using (10, 6*a*), is given by

$$\begin{aligned} \lambda &= \log(1 + 4F - 4F^2 - 12G^2) \\ &= 4F - 12F^2 - 12G^2 \end{aligned}$$

and (10, 7) reduces to

$$L = F - F^2 - G^2$$

or

$$L = \tfrac{1}{2}(\vec{B}^2 - \vec{E}^2) - \tfrac{1}{4}\{(\vec{B}^2 - \vec{E}^2)^2 + 4(\vec{B}\cdot\vec{E})^2\} \qquad (10, 8)$$

[19] The invariant G appears as square only, as pointed out by Weiss. See V, p. 89.

whereas the Lagrangian of Euler and Köckel is

$$L = \tfrac{1}{2}(\vec{B}^2 - \vec{E}^2) - \frac{1}{90\pi m^4 a}\left\{(\vec{B}^2 - \vec{E}^2)^2 + 7(\vec{B}\,\vec{E})^2\right\} \qquad (10, 9)$$

and Born's Lagrangian is

$$L = \tfrac{1}{2}(\vec{B}^2 - \vec{E}^2) - \tfrac{1}{8}\{(\vec{B}^2 - \vec{E}^2)^2 + 4(\vec{B}\,\vec{E})^2\}. \qquad (10, 10)$$

From the above equations it is clear that while (10, 8) and (10, 10) agree in the second order terms in G, neither of them coincides with (10, 9). Also (10, 8) gives the estimate $1/a \simeq 130$, as done by Infeld's action-function ($\gamma = 0$).

11. Coincidence with the Lagrangian of Euler and Köckel.

The question that now arises is whether it is possible to manipulate the action-function so as to obtain the coincidence with (10, 9) with the further restriction that it should reduce itself to the Hoffmann-Infeld action-function when $\mu \to 0$. Now, it can be shown that, if we alter the second term of (10, 2) by multiplying or dividing with the factor $\cos \tfrac{1}{2}\mu$, the relations between the invariants F, G, P, Q will not be algebraic. Since this is desirable on grounds of simplicity, we can try with

$$T = \frac{e^{\lambda/2}}{\cos \tfrac{1}{2}\mu} - \frac{\lambda}{2} - f(\cos \tfrac{1}{2}\mu), \text{ such that } f(x) = 1, \text{ for } x = 1$$

or

$$T = \frac{e^{\lambda/2}}{\cos \tfrac{1}{2}\mu} - \frac{\lambda}{2} - f(\nu), \quad \nu = \cos \tfrac{1}{2}\mu. \qquad (11, 1)$$

We have $R = T_\lambda = \dfrac{e^{\lambda/2}}{2\cos \tfrac{1}{2}\mu} - \tfrac{1}{2}$; and $e^{\lambda/2} = (1 + 2R)\cos \tfrac{1}{2}\mu$ (10, 4)

$$T_\mu = \frac{e^{\lambda/2}\sin \tfrac{1}{2}\mu}{2\cos^2 \tfrac{1}{2}\mu} + \frac{f'(\nu)\sin \tfrac{1}{2}\mu}{2}.$$

$$L = 2R - \tfrac{1}{4}\lambda + \tfrac{1}{2}\{1 - f(\nu)\} \qquad (11, 2)$$

In consonance with (10, 6*a*), we assume the power-series expansions upto the second order

$$\begin{aligned} R &= F - 2F^2 + \alpha G^2, \\ \cos \tfrac{1}{2}\mu &= 1 + \beta G^2, \\ f(\nu) &= 1 + l G^2, \\ f'(\nu) &= k + k' G^2. \end{aligned} \qquad (11, 3)$$

From (6, 8)–(6, 9), the expressions for F and G are given by

$$\left.\begin{aligned} 2F &= (1 + 2R)^2 - (1 + 2R)\cos^2 \tfrac{1}{2}\mu + (1 + 2R) f'(\nu) \sin^2 \tfrac{1}{2}\mu \cos \tfrac{1}{2}\mu \\ -2G &= (1 + 2R) f'(\nu) \sin \tfrac{1}{2}\mu \cos^2 \tfrac{1}{2}\mu + (1 + 2R) \sin \tfrac{1}{2}\mu \cos \tfrac{1}{2}\mu \end{aligned}\right\} (11, 4)$$

Substituting (11, 3) in (11, 4) wherein we take the second equation after squaring both sides, and comparing coefficients, we have

$$\begin{aligned} \beta &= -2/(k + 1)^2 \\ \alpha &= -2/(k + 1) \end{aligned} \qquad (11, 5)$$

From (10, 4) we find λ, and substitute for λ, R and $f(\nu)$ in (11, 2) obtaining

$$I_1 = F - F^2 + G^2(\alpha - \tfrac{1}{2}\beta - \tfrac{1}{2}l). \qquad (11, 6)$$

If (11, 6) should coincide in the factor of G^2 with (10, 9) we should have

$$\alpha - \tfrac{1}{2}\beta - \tfrac{1}{2}l = -7/4$$

$$ie., \quad 2\beta + 2l - 4\alpha = 7 \qquad (11, 7)$$

We now still further specialise (11, 1) by putting $f(\nu) = \nu^n$, and determine the value of n so as to satisfy (11, 7).

If $f(\nu) = \nu^n = (1 + \beta G^2)^n = 1 + n\beta G^2$, to the first approximation

$f'(\nu) = n\nu^{n-1} = n(1 + \{n - 1)\, G^2\}$,,

Hence,

$$\left.\begin{aligned} l &= n\beta \\ k &= n \end{aligned}\right\} \qquad (11, 8)$$

Putting in (11, 5) and (11, 8) in (11, 7) we get the equation for n

$$\frac{8}{n+1} - \frac{4}{(n+1)^2} - \frac{4n}{(n+1)^2} = 7$$

or $$7n^2 + 10n + 3 = 0 \qquad (11, 9)$$

This equation gives $n = -1$ or $n = -3/7$; but $n = -1$ would make the values of α and β infinite, and consequently of R and $\cos \tfrac{1}{2}\mu$. Neglecting this value we can take $n = -3/7$ and obtain an action-function which has the desired coincidence of the Lagrangian.

In an exactly similar way, we can show that

$$T = e^{\lambda/2} \cos \tfrac{1}{2}\mu - \frac{\lambda}{2} - (\cos \tfrac{1}{2}\mu)^n,$$

where $n = 8/7$ also gives an action function of the desired type.

12. *Conclusion.*

It is practically certain that the method adopted in the previous article can be applied to several other action-functions so as to obtain the Lagrangian of the type searched for. It appears therefore that even this does not restrict the type of action-function; nor should this be surprising since we are merely comparing coefficients of particular terms in power-series expansions and not going on any general principle. Anyway it serves to bring out the possibilities of the field-theory.

THE REPLICATION OF AN EXPERIMENT.

Part I. Identical Samples from a Binomial Population.

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1. When we wish to get some information about a population, which is unknown or partly known, we perform a suitable experiment. The results obtained may be considered to be a random sample from that population. We try to extract as much of the required information as possible from the data. When the experiment is repeated independently we get another random sample. It is known that two independent samples from a population can give us more information about it than either can by itself. It is also known or rather believed that every time an experiment is repeated independently, that is to say in Statistical language every time a random sample is drawn from a population, it must be possible to extract more and more information about the population. This view is not, however, shared by some Statisticians for example, N. R. Campbell and Harold Jeffreys. According to the views expressed by the former in (1) it would appear that when we perform experiments to determine, say the ratio of the metre to the yard, the accuracy of our result increases with the first few experiments, that beyond a certain number of experiments the accuracy decreases, and that the best number of experiments to be performed should be left to the experimenter's judgment. Commenting on this Jeffreys says on p. 357 of (2) " On the whole I should agree with him ".

2. We have thus two divergent views on the same question, one in favour of a large number of experiments, and the other for restricting the number to a definite value which is left to the discretion of the experimenter. It seemed, therefore, useful to examine this question at least in a case in which the question can be definitely solved. Such a case has been partly considered on p. 231 of (3). We will discuss it in some detail here.

3. *The problem.*—There is a set of 12 coins. It is required to find out the nature (whether true or false) of the coins from merely a knowledge of the throws of this set.

The population (of the throws) in this case is only partly known in that we know that it is binomial, nothing else being known.

In the paper ([3]) it is shown how to extract relevant information about a binomial distribution from a sample from it. A second sample increases this information, but the calculations become somewhat laborious when the two samples are different. From the examples worked in ([3]) it can be easily seen that the tediousness and the laboriousness of the computations increase exceedingly quickly with every sample which yields a result different from all the previous samples. However, in the one case in which all the samples have given the same result, the calculations become as simple as that when there is a single sample. Although this case will occur exceedingly rarely in actual practice, we will consider it here not only because it can be solved completely and without much difficulty, but from the solution we see how exactly and to what extent our knowledge about the population increases with every sample in this particular case. Further this will also help us in gaining a good idea as to how in the general case, that is in the case in which no two samples yielded the same result, our knowledge about the unknown population advances with every repetition of the experiment. Hence, we will consider the special case in which every throw gave the same result.

Suppose the result of each throw is 4 heads and 8 tails. Before the first throw was made we could have made any one of the assumptions, namely, that all or a few or none of the 12 coins are true or have both heads or both tails. In fact, we could have chosen any one of these 91 possible hypotheses.

After seeing the first throw which gave us 4 heads and 8 tails, we know immediately that there cannot be more than 4 coins with both heads or more than 8 coins with both tails. This rules out 46 assumptions and we are left with 45.

So far we have not considered the effect of random chance. If we take this into account now, we will be able to exclude some more out of the remaining 45 hypotheses even when we know the result of only the first throw. The following will illustrate the method :—

Suppose we know that in each of m successive throws 4 heads and 8 tails are turned up. Let us make the assumption that b coins have both heads and n are true, the remaining $(12 - n - b)$ coins, of course, having both tails. We should see whether this assumption is valid. We may proceed as follows :

Since there are b coins with both heads, we are already assured of at least b heads in each throw. Hence it is a question of getting $(4 - b)$ heads from n true coins in each of m successive throws. If this could be obtained

by random chance, our assumption, that out of the twelve coins b have both heads and n are true, is valid.

Now, the chance of getting a head from a true coin is $\frac{1}{2}$. Hence the chance of getting not more than $(4 - b)$ heads from n coins in m successive throws is given by [see (3)]

$$P_1 = [I_{\frac{1}{2}}\ (n + b - 4,\ 5 - b)]^m \qquad \text{(i)}$$

Similarly taking the tails into consideration we get

$$P_2 = [I_{\frac{1}{2}}\ (4 - b,\ n + b - 3)]^m \qquad \text{(ii)}$$

where the I's are incomplete β-function ratios [see (4)].

Our hypothesis has to be rejected if either P_1 or P_2 is less than P, our limit for random chance. Instead of testing each of the remaining 45 hypotheses separately we can shorten the work very much by proceeding in the following manner :—

We rewrite (i) and (ii) as

$$I_{\frac{1}{2}}\ (n + b - 4,\ 5 - b) = P_1^{\frac{1}{m}} > P^{\frac{1}{m}} \qquad \text{(iii)}$$

$$\text{and } I_{\frac{1}{2}}\ (4 - b,\ n + b - 3) = P_2^{\frac{1}{m}} > P^{\frac{1}{m}} \qquad \text{(iv)}$$

We fix upon some value for P, say 0·05.

We start with $b = 0$, *i.e.*, with the assumption that there are no coins with both heads, and take $m = 1$. From the tables (4) we find the maximum value of n not exceeding 12 for which (iii) is satisfied. We get $n = 12$. Similarly, we find the least value of n for which (iv) is satisfied. This comes out as 4. This means that when none of the coins have both heads, the number of true coins may have any value from 4 to 12 so that we may get by random chance, the limit for which is 0·05, 4 heads and 8 tails in the first throw.

We now take $b = 1$ and find the two limits for n, and so on up to $b = 4$. The same working is repeated for values of $m = 2, 3, 4, \ldots$. The results are exhibited in the following table.

This table is self-explanatory. The last row corresponding to a throw gives the total number of possible hypotheses admissible after the result of that throw is known. Thus we see that the consideration of variation due to chance has further decreased the possible number of hypotheses from 45 to 39 after the result of the first throw is fully taken into account. The second throw enables us to diminish this number to 26 and so on.

After the seventh throw we see that when $b = 0$, n should neither be less than 8 nor greater than 7, which is absurd. This only means that there is no valid hypothesis corresponding to $b = 0$. (Hence the numbers 8 and 7

TABLE.

Assumed number of coins with both heads	Possible number of true coins in the set deduced after seeing the results of all throws up to and including that of throw number							
	1	2	3	4	5 & 6	7	8–10	11–∞
0	4–12	5–11	6–10	7–9	7–8	**8–7**	..	..
1	3–11	4—9	5—7	5–6	6	6	..	..
2	2–10	2—7	3—5	3–4	4	4	..	..
3	1—7	1—4	1—3	1–3	2	2	2	..
4	0—4	0—2	0—1	0–1	0	0	0	0
Total number of possible hypotheses	39	26	16	12	6	4	2	1

are given in thick type. Such numbers are omitted from the other columns.) Thus after the seventh throw we infer that there must be at least one coin with both heads. We are now left with the following four hypotheses :—

(1) 1 H^2, 6 HT and 5 T^2,*
(2) 2 H^2, 4 HT and 6 T^2,
(3) 3 H^2, 2 HT and 7 T^2,
(4) 4 H^2, 0 HT and 8 T^2.

The eighth throw knocks out the first two hypotheses, but it is not until the 11th throw that the third hypothesis is thrown out. After the 11th throw we can assert, on our 0·05 limit for random chance, that there are exactly 4 coins with both heads, 8 coins with both tails and no true coins at all. So that our knowledge of the set and hence that of the population of throws from it is complete and further experiments after the eleventh are, therefore, unnecessary.

It has been mentioned above that before the first experiment (throw) was made there were 91 hypotheses that we could have made about the set of 12 coins. The first experiment enabled us to diminish the number to 39, that is to say the first experiment increased our knowledge about the set. The second increased it still further and so on until we come to the sixth which did not add to our information. From the seventh experiment

* H^2 = a coin with both heads, HT = a true coin and T^2 = a coin with both tails.

our information again went on increasing till the eleventh when the information became complete on our 5% limit for random chance.

Putting the same thing in another manner we can say that the error in our result decreased from the first to the fifth experiment, no improvement resulted from the sixth, and from the seventh onwards the error again began to get smaller until it became zero after the eleventh experiment was performed. Thus we see that in the case considered here the error did not increase at all. This does not support the view held by Campbell and Jeffreys mentioned above. On the other hand, it clearly demonstrates the importance of replicating our experiment.

The case we have considered above is, from the point of view of calculations, the simplest, namely that in which each independent repetition of an experiment gave us the same result. The next simplest case is that in which the experiments give two different results. This case is under consideration, and the results will be published in due course.

Summary.

The importance of replicating an experiment is shown by the consideration of the following problem :—To find out the nature of the coins in a set of 12 from merely the results of throws. The case discussed is the simplest in which each throw is assumed to have given the same result, namely 4 heads and 8 tails. It is shown that, in general, each throw increases, but never decreases, the accuracy of our result. It is also seen that after 11 experiments (throws) our knowledge of the set becomes complete and thus further experiments become unnecessary when the limit for random chance assumed by us is 5 %.

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GENERALIZATION OF A THEOREM OF DAVENPORT ON THE ADDITION OF RESIDUE CLASSES.

By S. S. Pillai.

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(Communicated by Dr. S. Chowla.)

The object of this note is to prove the following

Theorem. Let M be a positive integer; let $a_1, a_2, \cdots, a_m$ be m different residue classes (mod. M); let $\beta_1, \cdots, \beta_n$ be n different residue classes (mod. M); let $\gamma_1, \gamma_2, \cdots, \gamma_l$ be all those different residue classes which are representable as

$$a_i + \beta_j \qquad (1 \leqslant i \leqslant m, \quad 1 \leqslant j \leqslant n),$$

Further let $d = \max.\ (\mathrm{M}, \beta_r - \beta_s)$,* $1 \leqslant r \leqslant n, \quad 1 \leqslant s \leqslant n, \quad r \neq s$.
Then

$$l \geqslant m + n - 1;$$

provided that $m + n - 1 \leqslant \dfrac{\mathrm{M}}{d}$ and otherwise, $l = \dfrac{\mathrm{M}}{d}$.

When M is a prime, $d = 1$. So Davenport's theorem† is a particular case of this. In an issue of this *Proceedings*, I. Chowla generalized Davenport's theorem in a different direction and applied it to $\Gamma(k)$ in Waring's problem. Following I. Chowla, I apply the theorem of the present paper to Waring's problem with polynomial summands.

The proof follows very closely Davenport's. So it is proved by induction on n.

For $n = 1$, there is nothing to prove.

Let $n = 2$. Consider

(A) $$\begin{cases} a_1 + \beta_1, a_2 + \beta_1, \cdots, a_m + \beta_1, \\ a_1 + \beta_2, a_2 + \beta_2, \cdots, a_m + \beta_2. \end{cases}$$

(1) $a_r + \beta \not\equiv a_t + \beta \pmod{\mathrm{M}}$,

otherwise $a_r \equiv a_t \pmod{\mathrm{M}}$.

(2) $a_r + \beta_1 \equiv a_t + \beta_2$

and $a_s + \beta_1 \equiv a_t + \beta_2$

are impossible; for otherwise, by subtraction

$$a_r \equiv a_s$$

which is against our assumption.

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* (a, b) stands for the greatest common factor of a and b.

† *The Journal of the London Mathematical Society*, **10**, Part I, No. 37.

(3) Hence, if there are only m residue classes in (A), $\alpha_r + \beta_1 \equiv \alpha_t + \beta_2$, where for every r there is one unique t. Therefore

$$\sum_{r=1}^{m} (\alpha_r + \beta_1) \equiv \sum_{s=1}^{m} (\alpha_s + \beta_2).$$

So $$m\beta_1 \equiv m\beta_2 \pmod{M}.$$

Consequently, $$m \equiv 0 \left(\text{mod. } \frac{M}{(M, \beta_2 - \beta_1)}\right).$$

Therefore when $n = 2$, $l \geqslant m + n - 1$, provided $m < \frac{M}{(M, \beta_2 - \beta_1)}$,

i.e., $$l \leqslant \frac{M}{(M, \beta_2 - \beta_1)}.$$

So we can suppose that $n > 2$ and that the theorem is true for all $n' < n$. We apply the theorem to the two sets of residue classes $\gamma_1, \gamma_2, \cdots, \gamma_l$; $\beta_1, \cdots, \beta_n$.

If $l \geqslant \frac{M}{(M, \beta_1 - \beta_n)}$, there is nothing to prove.

So we may suppose that $l < \frac{M}{(M, \beta_1 - \beta_n)}$.

Hence there are $l + 1$ residue classes in the set

$$\gamma_i + \beta_1 ; \gamma_i + \beta_n, i = 1, \cdots, l.$$

Therefore there is a class δ such that $\delta - \beta_1$ is a γ and $\delta - \beta_n$ is not. Since we can arrange $\beta_2, \cdots, \beta_{n-1}$ and also $\gamma_1, \cdots, \gamma_l$ in any order we please, we may suppose, without loss of generality, that there exists a suffix r, $1 \leqslant r < n$, such that

$$\delta - \beta_s = \gamma_s, \text{ for } 1 \leqslant s \leqslant r,$$

and $$\delta - \beta_t = e_t, \text{ for } r < t \leqslant n,$$

$$e_t \neq \gamma_u, \text{ for } r < t \leqslant n, \quad 1 \leqslant u \leqslant l.$$

We now observe that none of the residue classes $\gamma_s - \beta_t$ (where $r < t \leqslant n$, $1 \leqslant s \leqslant r$) is an α. For if so, we should have

$$\alpha + \beta_t = \gamma_s = \delta - \beta_s$$

i.e., $$\alpha + \beta_s = \delta - \beta_t = e_t.$$

But $\alpha + \beta_s$ is a γ.

Hence e_t would be a γ, which is not the case. Therefore the l' residue classes representable in the form $\alpha_i + \beta_t$ ($1 \leqslant i \leqslant m$, $r < t \leqslant n$) form a subset of γ's not containing $\gamma_1, \gamma_2, \cdots, \gamma_r$. Thus $l' \leqslant l - r$. But by our theorem with $n' = n - r$,

$$l' \geqslant m + (n - r) - 1,$$

provided $l' \leqslant \frac{M}{d'}$,

where $d' = \text{max. } (M, \beta_i - \beta_j)$, $i, j = r + 1, r + 2, \cdots, n$; $i \neq j'$.

In virtue of our hypothesis the last condition is satisfied.

Hence $l \geqslant m + n - 1$.

THE CONDENSATION OF ALDEHYDES WITH MALONIC ACID IN THE PRESENCE OF ORGANIC BASES.

Part IX. The Condensation of β-Hydroxynaphthaldehyde (2-Hydroxy-1-naphthaldehyde).

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and
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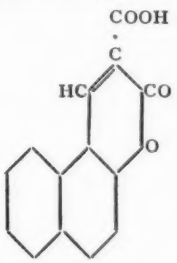
Received August 23, 1937.

The diminished yield of the condensation-product, when the aldehyde has a hydroxy-group in the *ortho*-position, has been noted in the earlier papers.[1] All the earlier observations have been based on the behaviour of aromatic aldehydes containing a benzene ring. In 2-hydroxy-1-naphthaldehyde or β-hydroxy-naphthaldehyde, we have an aldehyde with the aldehyde and the hydroxy groups in the *ortho*-position to each other but the ring is the condensed ring of naphthalene.

It is now found that in the presence of lutidine and α-picoline in traces, the yields are good, being above 80 per cent., while in the presence of pyridine, the yield is almost quantitative. Even when no base was used, but when the heating was exactly as before, the yield was over 60 per cent.

The product in all cases was identified, by melting-point as well as by other chemical properties, as 5·6-benzo-coumarin-3-carboxylic acid (or β-naphthocoumarin-α-carboxylic acid).



The aldehyde in question has been known for over half a century, having been prepared by various workers by different methods.[2] Gattermann's

method[3] has also been used for its preparation with various modifications. In the present case also, the same method was used as is now generally employed for the preparation of resorcylaldehyde, by the action of dry hydrogen chloride on a mixture of β-naphthol and zinc cyanide in dry ether.[4] The β-hydroxy-naphthaldehyde came out in good yield and gave all the tests described in literature (see below).

Several different condensations of this aldehyde have been recorded, notably with Perkin's reagents, aceto-acetic acid, cyanacetic ester, malonic acid and acetone-dicarboxylic acid respectively. Perkin's reaction has been tried by Kauffmann, who after heating the aldehyde at 180° for $2\frac{1}{2}$ hours in a sealed tube, with sodium acetate and acetic anhydride, obtained benzo-coumarin $C_{10}H_6\begin{matrix}CH=CH\\ |\\ O-CO\end{matrix}$ ([5]). By keeping the mixture for three days, Rousset reports having obtained in small quantities β-naphthylacrylic acid.[2] On heating similarly with sodium propionate and propionic anhydride, Bartsch obtained methyl-benzo-coumarin.[6] On heating, however, with malonic acid and glacial acetic acid,[7] or by applying Knoevenagel's reaction, *i.e.*, with malonic acid and aniline in alcoholic solution,[8] the product obtained was benzo-coumarin-carboxylic acid, as in our experiments.

Experimental.

Preparation of β-hydroxy-naphthaldehyde.—14·4 g. of β-naphthol (1/10th mole.) and 17·6 g. freshly prepared zinc cyanide (1/10th of 1·5 mole.) were added to 125 c.c. of dry ether and a current of dry hydrogen chloride was passed in for about three hours, rapidly at first and slowly later on, while the whole mixture was kept cooled by a freezing mixture. Stirring by mechanical means was not necessary as the bubbling of the hydrogen chloride did it efficiently. At the end the ether was decanted off from the solid and the solid as usual was decomposed by water.[4] The yield was 15 g. (about 87 per cent. of theory). On recrystallisation, the aldehyde came out as colourless crystals which, however, darkened on exposure. M.P. 81° C. (Literature gives 81°C., Rousset, Gattermann; and 82°C., Betti; Mundici, Bezdzik, Friedländer; *loc. cit.*). It was easily soluble in aqueous alkali, but very insoluble in water, reduced ammoniacal silver, giving a silver mirror, and gave a brown precipitate with ferric chloride solution (as noted by Kauffmann), though it did not reduce Fehling's soltuion (compare Fosse, *loc. cit.*). It was soluble in alcohol and ether (compare Rousset).

Condensation of the aldehyde with malonic acid in the presence of organic bases.—1·72 g. β-hydroxy-naphthaldehyde and 1·04 g. malonic acid (1/100th of a mole.) and 0·12 c.c. (0·15 mole. proportion) were heated on the water-bath for 12 hours. The solid product obtained was not completely soluble in sodium carbonate solution; it was dissolved in tepid 2N NaOH solution, and the resulting solution treated with concentrated hydrochloric acid, when the benzo-coumarin-carboxylic acid was precipitated and was then recrystallised from alcohol or acetone. It came out as yellow needles and melted at 234° C. (*cf.* 234°C., Bartsch; 233°C., dec., Betti and Mundici; 232°C., Knoevenagel and Schröter; *loc. cit.*, 234–235°C., Sacho and Brigl[9]). In alcoholic solution it gave a characteristic yellow-blue fluorescence (Bartsch, Betti, Mundici), and with concentrated sulphuric acid it gave an intensive yellow colouration (Knoevenagel and Schröter). The yield was 2·2 g. or 92 per cent.

With α-picoline (0·14 c.c.) in place of pyridine, under the same conditions, the product was the same and the yield 2 g.

With lutidine (0·16 c.c.), the product and the yields remained the same (2 g).

When the heating temperature was slightly raised, *i.e.*, was 105°–110° C., an 83 per cent. yield was obtained with pyridine in much less time, in only four hours, and 92 per cent. in six hours.

Condensation without a base.—Under this condition, the condensation still took place, giving, on six hours' heating at 105°–110°C., the same product in 62·5 per cent. yield (1·5 grams).

Summary.

It is clear that the hydroxy group in 2-hydroxy-1-naphthaldehyde does not give the same difficulty as was given by it in salicylaldehyde, and can be condensed with malonic acid with or without any organic base, but the reaction is accelerated as usual by traces of organic bases, and the product then comes out in almost quantitative yields. It may be stated that the aldehyde obtained similarly from α-naphthol has so far resisted completely all attempts at condensation with malonic acid under the usual conditions, only dark resin being obtained so far.

The authors' thanks are due to the Education Department of the Government of the United Provinces of Agra and Oudh for the grant of a research scholarship which has enabled one of them (T. A. V.) to take part in this work.

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HETEROCYCLIC COMPOUNDS.

Part. IV. Coumarins from Resacetophenone and Ethylacetoacetate and Synthesis of Coumarino-γ-Pyrones.

By R. D. Desai and Shaik Abdul Hamid.
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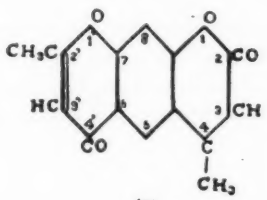
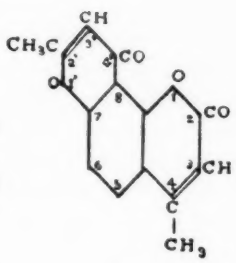
(Communicated by Dr. R. K. Asundi, M.Sc., Ph. D.)

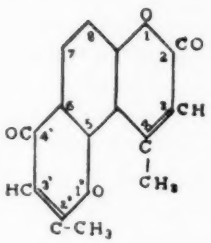
Coumarino-α-pyrones and chromono-γ-pyrones are known in literature,[1] but there does not seem to be any record of the synthesis of coumarino-γ-pyrones which can exist in three different types (I, II and III), if the central benzene nucleus is derived from resorcinol. The starting materials for their synthesis are the *o*-hydroxy-acylcoumarins which can be made to undergo the Kostanecki Reaction[2] to build up the chromone ring. One such compound is 4-methyl-7-hydroxy-8-acetylcoumarin, and an elegant method for its preparation has been worked out by Limaye,[3] by the Fries Transformation of 4-methyl-7-acetoxycoumarin. An isomeric compound melting at 210°C. was also isolated in a very small yield during the course of this reaction, and this was shown by Limaye and Gangal[4] to be 4-methyl-7-hydroxy-6-acetylcoumarin.



(I)



(II)



(III)

With a view to preparing coumarins of this type, we studied the action of acid chlorides on 7-hydroxy-4-methylcoumarin in the presence of anhydrous aluminium chloride in nitrobenzene or acetylene tetrachloride solution without any success. Similar negative results were obtained with 7-methoxy- and 7-acetoxy-4-methylcoumarins.

In passing it must be observed that 7-methoxy-2-methylchromone did not condense with acetylchloride in the presence of aluminium chloride.

The next method tried was the Pechmann Condensation of resacetophenone with ethylacetoacetate, but the condensation did not proceed in the presence of concentrated sulphuric acid, 73 per cent. sulphuric acid, syrupy phosphoric acid, and sodium ethoxide. Phosphorus oxychloride, however, gave a coumarin melting at 210°C. and this was identified as 4-methyl-7-hydroxy-6-acetylcoumarin by comparing it with a specimen prepared by the method of Limaye and Gangal (*loc. cit.*).

As this interesting coumarin was now readily available, we studied some of its properties. Monobromination in glacial acetic acid or chloroform solution gave a product melting at 216°C., which was presumably 3-bromo-4-methyl-6-acetyl-7-hydroxy coumarin, because on boiling with a normal sodium carbonate solution, according to the method of Fitting and Ebert,[5] 3-methyl-5-acetyl-6-hydroxycoumarilic acid and 3-methyl-5-acetyl-6-hydroxycoumarone, together with a small amount of a substance melting at 230°C., and soluble in sodium carbonate, but insoluble in sodium bicarbonate solution were obtained. The constitution of this product is under investigation. When 4-methyl-6-acetyl-7-methoxycoumarin was brominated, either monobromo- or dibromo-derivatives were formed, but on treating them with alkali, extremely complicated and puzzling results were obtained, and we hope to publish them later on.

Vigorous acetylation of 4-methyl-6-acetyl-7-hydroxycoumarin gave a product melting at 245°C. together with the acetyl derivative of the original coumarin. The new product is presumably the 4 : 2'-dimethyl-3'-acetyl-coumarino-(7 : 6)-γ-pyrone (see Formula I). Similarly 4-methyl-7-hydroxy-8-acetylcoumarin reacted with acetic anhydride in the presence of anhydrous sodium acetate giving 4 : 2'-dimethyl-3'-acetyl-coumarino-(7 : 8)-γ-pyrone (Formula II) together with small amounts of two other products melting at 300°C. and 320°C., but we cannot express our views regarding their nature owing to insufficient data. As these coumarino-γ-pyrones have also been prepared by Limaye and Gangal (*loc. cit.*), we do not wish to press this portion of our investigation further.

The condensation of resacetophenone with β-ketonic esters in the presence of phosphorus oxychloride is a reaction of wide application, and we are busy studying the action of this dihydroxy-ketone as well as its substitution products on other open-chain, as well as cyclic-β-ketonic esters.

Experimental.

Preparation of 4-methyl-6-acetyl-7-hydroxy-coumarin.—A mixture of resacetophenone (8 g.), acetoacetic ester (6 g.) and phosphorus oxychloride (2 g.) was heated on the water-bath for six hours when the evolution of

hydrogen chloride ceased. The residue was extracted with three lots of benzene (40 c.c. each) and the benzene extracts were combined. After distilling off the solvent, the residue was crystallised from alcohol (animal charcoal) when colourless, flat needles melting at 210°C. were obtained (yield 40 per cent.). [Found : C, 65·7 ; H, 4·8 ; $C_{12}H_{10}O_4$ requires C, 66·0 ; H, 4·6 per cent.]

It was soluble in sodium hydroxide as well as sodium carbonate solution giving a yellow colour, and a weak, violet fluorescence. Concentrated sulphuric acid dissolved it with a yellow colour. Its alcoholic solution gave a reddish violet colouration with ferric chloride solution. The *benzene insoluble portion* was a black colouring matter, sparingly soluble in hot alcohol and did not melt upto 300°C. It dissolved in alkali with a deep-red colour, and was recovered unchanged on acidification with hydrochloric acid.

The acetyl derivative was obtained by boiling it (0·5 g.) with acetic anhydride (5 c.c.) and a few drops of pyridine on a sand-bath for two hours, and crystallised from dilute alcohol in long, fine needles melting at 180°C. (Limaye and Gangal give 172°C.) *The semicarbazone* obtained by boiling the alcoholic solution of the coumarin with semicarbazide acetate on a water-bath for four hours, crystallised from alcohol in small needles melting at 320°C. [Found : C, 56·5 ; H, 4·7 ; $C_{13}H_{13}O_4N_3$ requires C, 56·7 ; H, 4·7 per cent.]

The methyl ether was obtained by dissolving the coumarin (1 g.) in caustic soda (8 c.c.) and gradually adding dimethylsulphate (2·3 c.c.). The solid that separated out was filtered off, and crystallised from dilute alcohol in needles melting at 212°C. (Limaye and Gangal give 210°C.) and was depressed to 180°C. by the parent substance.

If the period of methylation is prolonged, and a stronger alkali is used, copious evolution of carbon dioxide takes place, and a product melting at 148°C. separates out. The nature of this change is under investigation.

Preparation of 4-methyl-6-acetyl-7-hydroxy-coumarin by Fries Transformation of 4-methyl-7-acetoxycoumarin.—Limaye and Gangal's method was modified as follows :—4-methyl-7-acetoxycoumarin (10 g.) and aluminium chloride (30 g.) were intimately mixed by grinding in a mortar, and the mixture heated in an oil-bath at 140°–150°C. for about an hour. After cooling, the aluminium chloride was decomposed by dilute hydrochloric acid, and the solid that separated out was filtered off. It was dissolved in a warm 5 per cent. sodium bicarbonate solution and the insoluble portion was rejected. The solid obtained on acidification with hydrochloric acid was dried, and extracted with benzene which left undissolved much of the

4-methyl-7-hydroxy-coumarin. Benzene was now driven off, and the residue crystallised from dilute alcohol when long, fine needles melting at 168°C. were obtained. The alcoholic mother-liquor gave a second fraction of the same substance, but it was slightly impure. One recrystallisation sufficed to purify it. The alcohol was now removed from the mother-liquor, and the residue was constantly shaken in the cold with 5 per cent. sodium bicarbonate solution. The residue was crystallised from dilute alcohol when after two or three crystallisations, flat needles melting at 210°C. were obtained. Its melting point was not depressed by the product obtained by condensing resacetophenone with acetoacetic ester in the presence of phosphorus oxychloride (yield 4-5 per cent.).

3-Bromo-4-methyl-6-acetyl-7-hydroxycoumarin.—To a solution of 4-methyl-6-acetyl-7-hydroxycoumarin (3 g.) in glacial acetic acid (30 c.c.), bromine (1·6 c.c.) dissolved in glacial acetic acid (5 c.c.) was slowly added, and kept overnight after exposure to sunlight. The solid obtained by diluting the solution freely with water was collected, and crystallised from glacial acetic acid, when long needles melting at 216°C. were obtained. [Found: Br, 26·6; $C_{12}H_9O_4Br$ requires Br, 26·9 per cent.]

The acetyl derivative crystallised from dilute alcohol in needles melting at 195°C. [Found : Br, 23·8; $C_{14}H_{11}O_5Br$ requires Br, 23·6 per cent.]

Hydrolysis of the bromo product by sodium carbonate solution.—A solution of the bromo-coumarin (2·5 g.) in 5 per cent. sodium carbonate solution (45 c.c.) was heated on sand-bath under reflux for two hours. The *solid A* that separated out on cooling was filtered off, and the solution acidified with concentrated hydrochloric acid. The solid thus obtained was treated with 4 per cent. sodium bicarbonate solution when much of it dissolved, leaving a small *residue* which was soluble in sodium carbonate or sodium hydroxide, and crystallised from dilute alcohol in small needles melting at 230°. This is under investigation. The sodium bicarbonate soluble portion was recovered after acidification with concentrated hydrochloric acid and crystallised from dilute alcohol when *3-methyl-5-acetyl-6-hydroxy-coumarilic acid* was obtained in small needles melting at 260°C. (decomp.). [Found : C, 61·3; H, 4·4; $C_{12}H_{10}O_5$ requires C, 61·5; H, 4·3 per cent.]

The solid A which separated out from sodium carbonate solution crystallised from dilute alcohol in long, fine needles melting at 138°C. It was *3-methyl-5-acetyl-6-hydroxy-coumarone* because the same product was obtained by decarboxylation of the coumarilic acid. [Found: C, 69·7; H, 5·5; $C_{11}H_{10}O_3$ requires C, 69·5; H, 5·3 per cent.]

Its alcoholic solution gave a bluish-green colouration with ferric chloride solution.

The acetyl derivative prepared in the usual manner crystallised from alcohol in small plates melting at 118°C. [Found : C, 67·0 ; H, 5·3 ; $C_{13}H_{12}O_4$ requires C, 67·2 ; H, 5·2 per cent.]

The methyl ether crystallised from hexane in needles melting at 94°C. [Found : C, 70·3 ; H, 6·0 ; $C_{12}H_{12}O_3$ requires C, 70·6 ; H, 5·9 per cent.]

The semicarbazone crystallised from alcohol in scales melting at 315°C. (decomp.). [Found : C, 58·1 ; H, 5·2 ; $C_{12}H_{13}O_3N_3$ requires C, 58·3 ; H, 5·3 per cent.]

Monobromo- and dibromo-derivatives of 4-methyl-6-acetyl-7-methoxy-coumarin.—A solution of bromine (0·5 c.c.) in glacial acetic acid (5 c.c.) was added to the solution of methoxycoumarin (1 g.) in glacial acetic acid (10 c.c.), and exposed to sunlight. After keeping overnight, the solid obtained by diluting the mixture with water was collected, and crystallised from alcohol when fine silky needles of the monobromo-methoxycoumarin melting at 165°C. were obtained. [Found : Br, 25·3 ; $C_{13}H_{11}O_4Br$ requires Br, 25·7 per cent.]

The dibromo-derivative was obtained in an identical manner by using double the amount of bromine. It crystallised from dilute alcohol in fine, silky needles melting at 207°C. [Found : Br, 40·9 ; $C_{13}H_{11}O_4Br_2$ requires Br, 41·0 per cent.]

The Kostanecki Reaction with 4-methyl-6-acetyl-7-hydroxycoumarin and synthesis of 4 : 2'-dimethyl-3'-acetyl-coumarino-(7 : 6)-γ-pyrone.—A mixture of the above coumarin (2 g.), acetic anhydride (15 c.c.) and anhydrous sodium acetate (5 g.) was heated in an oil-bath at 170°-180°C. for ten hours. The solid obtained by pouring the mixture into water was collected, and treated with a warm solution of 4 per cent. sodium bicarbonate for two hours to remove the unreacted material. *The coumarino-γ-pyrone* crystallised from boiling alcohol in pale-yellow needles melting at 245°C. (yield 0·6 g.). [Found : C, 67·4 ; H, 4·3 ; $C_{16}H_{12}O_5$ requires C, 67·6 ; H, 4·2 per cent.]

The substance dissolved in sodium hydroxide and sodium carbonate on warming. Its solution in concentrated sulphuric acid was yellow. The alcoholic mother-liquor, on concentration gave another substance melting at 175°C. and this was identified as the acetyl-derivative of 4-methyl-6-acetyl-7-hydroxycoumarin (m.p. 180°C.).

The Kostanecki Reaction with 4-methyl-7-hydroxy-8-acetylcoumarin and synthesis of 4 : 2'-dimethyl-3'-acetyl-coumarino-(7 : 8)-γ-pyrone.—The mixture of the coumarin (2 g.), acetic anhydride (15 c.c.) and anhydrous sodium acetate (5 g.) was heated in an oil-bath at 175°-180°C. for ten hours. The solid obtained by decomposing the mixture was filtered off, and treated with a warm sodium bicarbonate solution to remove the unchanged coumarin.

The *residue* was extracted with alcohol which dissolved everything leaving a small portion which crystallised from glacial acetic acid in pale-yellow micro-crystalline needles melting at 320°C. [Found : C, 69·3 ; H, 4·3; $C_{14}H_{10}O_4$ requires C, 69·4 ; H, 4·1 per cent.] It dissolved in sodium hydroxide on warming, and gave yellow solution when dissolved in concentrated sulphuric acid.

The alcoholic solution deposited a micro-crystalline solid melting at 300°C. Its melting point was depressed by the product melting at 320°C. [Found : C, 69·5 ; H, 4·1 ; $C_{14}H_{10}O_4$ requires C, 69·4 ; H, 4·1 per cent.]

It was soluble in alkali on warming and also in concentrate sulphuric acid with a yellow colour. On concentration, the mother-liquor gave small plates melting at 260°C. ; and its melting point was depressed by both the products melting at 300°C. and 320°C. It dissolved in sodium hydroxide on warming, and was also soluble in concentrated sulphuric acid with a yellow colour. [Found : C, 67·5 ; H, 4·2 ; $C_{11}H_{12}O_4$ requires C, 67·6 ; H, 4·2 per cent.] This compound was, presumably, the *coumarino-γ-pyrone*.

Summary.

Resacetophenone condenses with acetoacetic ester in the presence of phosphorus oxychloride giving 4-methyl-6-acetyl-7-hydroxycoumarin. Coumarino-γ-pyrones have been prepared by the Kostanecki Reaction with this coumarin, as well as its 8-acetyl isomer.

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STUDIES IN THE CONESSINE SERIES.

Part III. Degradation of Conessine and *Iso*-Conessine Hydroiodides to a Common Hydrocarbon.

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In the course of studies in the comparative N-stability of conessine and *iso*-conessine[1] it was noted that the latter is quantitatively recovered on its Hoffmann degradation and that in contrast to conessine, it cannot be thereby degraded to a hydrocarbon or a base corresponding to apo-conessine[2] $C_{21}H_{29}N(CH_3)_2$.[3]

In so far as N-stability has been found to depend in bases on the position of a double bond in a radical and the state of tension in it in the β-λ position to N,[4] we considered it quite probable that the increased N-stability of the *iso*-conessine nucleus should be due to a shifting of the double bond (through the action of conc. sulphuric acid. on conessine), attended with a decrease of tension in this position. If this were so, *iso*-conessine should yield dihydroconessine on hydrogenation of its double bond. It appears, however, that *iso*-conessine is even more difficult to hydrogenate than conessine[5] and it was not so far possible for us to get a uniform hydroproduct through its catalytic reduction with Pt black. It has, however, been possible to largely establish this point by the degradation of the hydroiodides of conessine and *iso*-conessine to a common hydrocarbon, $C_{21}H_{30}$, ($d = 1{\cdot}0109$; $n_D^{35°} = 1{\cdot}5515$; $a_D^{31°} = +35°$) in so far as the two fresh double bonds noted in it can be assumed to have taken positions which remove this cause of isomerism.

Experiments in the bromination of the hydrocarbon lead to the conclusion that it is easily brominated at one of the double bonds, less so at the second, while the third double bond is not completely saturated with bromine, the final Br values corresponding to about 5 as against 6 atoms of bromine. The molecular refraction found for the hydrocarbon does,

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[1] Siddiqui, Siddiqui and Sharma, *Proc. Ind. Acad. Sci.*, 1936, 283.
[2] Kanga, Aiyar and Simonsen, *J. Chem. Soc.*, 1926, 2123.
[3] Spaeth and Hromatka, *Ber.*, 1930, **63**, 125.
[4] V. Braun, *Ber.*, 1902, **35**, 1279 ; 1926, **59**, 1081 and preceding papers.
[5] Spaeth and Hromatka, *loc. cit.*

however, further signify the presence of 3 double bonds in its molecule. [Found : MR, 89·16 ; $C_{21}H_{33}$ (with 3/=), requires MR, 89·39.] It may thus be considered as isomeric with the hydrocarbon obtained by Spaeth and Hromatka ($C_{21}H_{30}$ (3/=) ; $a_D^{15°} = -183·7$; $d^{15°} = 0·989$) through the reductive degradation of apo-conessine after Emde (*loc. cit.*).

The work so far done on the constitution of conessine shows that the clarification of this problem will largely depend on the thorough investigation of its carbocyclic nucleus. The low yields of apo-conessine and finally of the hydrocarbon from it, and also the long protracted process that eventually leads to it, make Spaeth's hydrocarbon a very unsatisfactory starting material for this purpose. As the hydrocarbon obtained by us, which we provisionally propose to call conessen (reserving the name conessan for the fully hydrogenated hydrocarbon), is obtained in a single step from conessine, we made especial efforts to increase its yield, which we finally succeeded in raising up from 30% in the initial experiments to 75% of theory by the method noted in the Experimental.

Apart from isolating the hydrocarbon, we have noted that the nitrogen is chiefly split off as ammonia which we could actually isolate as ammonium chloride in a yield amounting to 13% of the degraded conessine hydroiodide as against 17% calculated for both the nitrogen atoms in conessine. A modified Herzig and Meyer estimation of methyl iodide, evolved on heating conessine hydroiodide, gave values corresponding to about one methyl iodide to one molecule of conessine.

The degradation of conessine and *iso*-conessine hydroiodide appears to proceed in too complicated a manner to be expressed by an equation. The observations made in this regard, however, indicate that HI, present in the salt, acts as a demethylating and a reducing agent, and that an unsaturated hydrocarbon, probably ethylene, is produced in the process, which could not be definitely fixed up, but whose presence is indicated by the reducing action of the gases evolved on a solution of $KMnO_4$ as well as platinic chloride.

The dry distillation of conessine and *iso*-conessine was also tried with, and without dehydrogenating agents (Pd and Se) in an attempt to get a simpler base, containing the ring nitrogen intact, but they both invariably gave non-nitrogenous products, apparently hydrocarbons, which, however, could not be sufficiently purified from the small quantities worked. As the yields in this case were comparatively low owing to resinification, the degradation of the bases under these conditions was not tried on a larger scale.

Experimental.

Degradation of conessine hydroiodide.—8·3 g. of conessine hydroiodide (m.p. 308°) were slowly melted in hydrogen atmosphere, in a distilling flask connected with a receiver leading into a 10% HCl trap, by carefully heating the flask from the top downwards, so that the sublimation of the hydroiodide to the cooler parts of the flask was kept to a minimum. Heating was stopped when the hydroiodide had completely melted down to a slightly reddish liquid and no more frothing or effervescence was noticeable in the molten mass.

The reddish yellow oil which had collected in the receiver was extracted with petroleum ether in which it was completely soluble. The straw coloured granular residue which did not dissolve in petroleum ether was found to be sublimed conessine hydroiodide (1 g.), from its melting point and mixed melting point with pure conessine hydroiodide.

The dark red brittle residue in the flask was also extracted out with petroleum ether, which left some darkish resinified impurities undissolved. The combined oil from the petroleum ether extracts of the flask and the receiver was fractionally distilled under reduced pressure, when the major fraction distilling at 243–48°/4·5 mm. was obtained as a pale yellow fluorescent oil. The yield of conessen thus obtained (2·5 g.), amounted to 71% of theory as calculated after deducting the unchanged conessine hydroiodide noted above.

The contents of the HCl catch gave 0·93 g. residue which proved to be exclusively NH_4Cl—12·7%on the weight of conessine hydroiodide degraded. In a second experiment 0·9282 g. of conessine hydroiodide was heated in CO_2 current in a Herzig and Meyer apparatus for $N\text{–}CH_3$ estimation. 0·3410 g. AgI was thereby obtained, equivalent to 25·6% of CH_3I on the weight of the degraded conessine hydroiodide, as against 46·5% required for 2 CH_3I. In another experiment the gases were successively led through platinic chloride and 1% $KMnO_4$ solutions after passing through an HCl catch. Considerable decolouration of $KMnO_4$ was noticed. The platinic chloride solution did not give any crystalline precipitate on concentration but was reduced on boiling for sometime.

Conessen ($C_{21}H_{30}$) distilled at 185–92°/3 mm. In 1% absolute alcoholic solution it showed $a_D^{31°} = +35·0°$; $d^{38°} = 1·0109$; $n_D^{35°} = 1·5520$. (After drying to constant weight at 50° *in vacuo* over P_2O_5 it gave: C, 88·9, 89·2°; H, 10·6, 10·6; M.W. cryoscopic in benzene 282; $C_{21}H_{30}$ requires C, 89·4; H, 10·6; M.W. 282.)

Bromination.—On direct titration of 0·1410 g. of conessen against a standard Br_2 solution in chloroform and following the titration with starch KI paper, it was found to take 0·085 g. of bromine (one double bond requires 0·080 g. bromine).

In a second experiment 0·092 g. conessen was put in cold with 0·1582 g. of bromine (3 double bonds require 0·156 g.) in glacial acetic acid solution. After a few hours, excess of bromine was back titrated against standard thiosulphate, when 0·095 g. of bromine was found to have been absorbed (2 double bonds require 0·1052 g.).

In another experiment 0·0296 g. conessen was kept overnight in cold with 0·0952 g. of bromine (large excess over 3 double bonds) in glacial acetic acid solution. On back titration of the excess it was found that 0·0425 g. bromine had been used up (3 double bonds require 0·050 g.; 2 double bonds require 0·0333 g.).

Degradation of iso-*conessine hydroiodide : conessen.*—*Iso*-conessine hydroiodide was heated and its degradation products worked up as in case of conessine hydroiodide, when it gave a hydrocarbon (75% of theory) and ammonia as ammonium chloride in the HCl catch, corresponding to 50% of theory. The hydrocarbon distilled at 240–46°/4·5 mm. as a pale yellow fluorescent oil like conessen obtained from conessine hydroiodide. In 1% absolute alcoholic solution it showed $a_D^{31°} = +33·5°$; $d^{38°} = 1·0109$; $n_D^{35°} = 1·5515$. (After drying to constant weight at 50° *in vacuo* over P_2O_5 found : C, 89·4 ; H 10·6 ; M.W.—cryoscopic in benzene, 290 ; $C_{12}H_{30}$ requires C, 89·4 ; H, 10·6% ; M.W. 282.) On bromination, 0·0397 g. of this hydrocarbon, kept overnight in cold with 0·0952 g. of bromine in glacial acetic acid solution, was found on back titration of the excess of bromine to have absorbed 0·0562 g. bromine (required for 3 double bonds 0·0680 g.) It thus appeared to be identical with conessen.

A COMBINED ELECTROMETER AND THERMIONIC VOLTMETER.

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Abstract.

Design data are given for a thermionic voltmeter which can also be used as an electrometer. The A.C. ranges are 0—6 and 0—10 volts R.M.S., the D.C. ranges 0—3 and 0—6 volts. The input capacity and resistance compare favourably with the best commercial instruments.

Introduction.

The thermionic valve is being increasingly used in general physical measurements and it is thought that a description of the design and performance of a combined portable electrometer and thermionic voltmeter might be of interest. The circuit used is due to Hoare[1] and slightly modified to suit the apparatus chosen. The instrument is in the form of a direct current bridge (Fig. 1) and aims at eliminating changes in calibration due

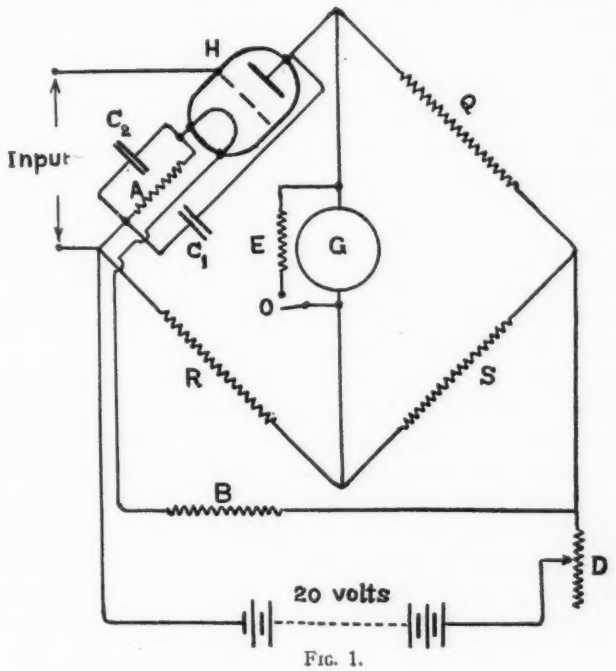

Fig. 1.

to small fluctuations in battery voltages. The D.C. plate resistance of the valve is balanced for zero volts input by a suitable choice of the resistances Q, R and S. Any voltage applied to the grid changes the D.C. plate resistance, unbalances the bridge or forces current through the microammeter. Grid bias is produced by the voltage drop across resistance A, while B is chosen to give the correct filament voltage. D is a rheostat to bring the instrument to the calibrated conditions before readings are taken.

Design Considerations.

The valve used was an Osram Electrometer type T, nominal rating :— anode voltage 4—10 volts, filament 1·0 volt, 0·1 amp. Insulation between grid and other electrodes 10^{15} ohms, capacity 1·6 micro-micro farads. In order to give as large a range as possible the anode and grid voltage were kept reasonably high without exceeding the nominal ratings. The total voltage supply necessary in this case is about 20 volts supplied by two small 10-volt H.T. accumulator units.

In order to make the scale more linear Moullin[2] has suggested the incorporation of a fairly high resistance in the anode circuit. This is done by making Q and S each 10,000 ohms. The condenser C_1 has a capacity of 2·0 microfarads in order to bypass the alternating component of anode current. C_2 is a small mica condenser across the grid biasing resistance to bypass stray currents when the instrument is used on high frequencies. The microammeter (Electradix) (G) has a range of 0—50 microamperes. The other resistances have the following values :—

R = 500,000 ohms, A = 100 ohms, B = 80 ohms, D = 60 ohms variable, E = 700 ohms.

Resistances Q, R and S are of the carbon type. It would probably be better to use wire wound resistances but as the currents passing are so small no ill-effects on the calibration have yet been noticed owing to their use. Resistances A and B are wound on a mica card.*

The valve (H) is mounted in a large brass screen (I, Fig. 2), the grid terminal (J) projecting through the end and connected through a large hole (K) in the top panel to a standoff terminal. The valve is in this way protected from mechanical damage and also in the dark which is a condition for highest insulation. The guard rings on the valve were connected to the negative end of the filament. The remainder of the components were arranged round the valve as shown in the figure.

* Lettering of Fig. 1 and Fig. 2 corresponds.

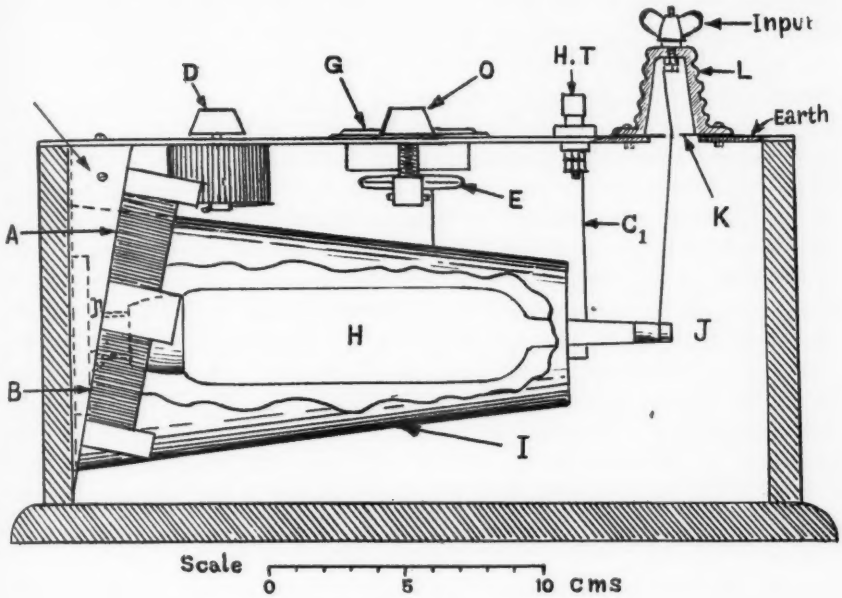

FIG. 2.

Before calibrating the meter the pointer of the microammeter was brought to the zero mark by adjusting the resistance D with the input terminals short circuited. After calibrating, whenever readings are to be taken the above adjustment reproduces the calibration conditions. The instrument was calibrated on 50 cycle A.C. against a commercial thermionic voltmeter using a potentiometer, and also on D.C. using an ordinary voltmeter. The ranges on A.C. are 0—6 and 0—10 volts R.M.S. and on D.C. 0—3 and 0—6 volts. The scales are reasonably linear.

Characteristics.

The two most important characteristics of a thermionic voltmeter are the apparent resistance due to grid current, and the input capacity.

The input capacity was measured by the following arrangement. A standard variable condenser was connected across the tuned circuit of a valve oscillator, which was tuned into the zero beat position on a receiver fitted with a beat frequency oscillator. The voltmeter was then connected in parallel with the standard condenser and the change in capacity of the standard necessary to give the zero beat condition was the input capacity of the voltmeter. Results gave an input capacity of 4·9 micro-micro farads

between the standoff and earth and 2·8 micro-micro farads as the capacity measured directly between the grid terminal of the valve and earth.

The grid current on such a valve is extremely small. Using a galvanometer sensitive to 0·05 microampere, no grid current was detected on the D.C. ranges, and on the A.C. ranges the valve only commenced to draw grid current when the applied potential exceeded 8·0 volts. Actually, on most of the ranges there appeared to be a slight inverse current but as it was at the limit of measurement, in order to get a better idea of the losses due to grid current the following experiment was performed. A 0·1 microfarad standard mica condenser was connected between the input terminals of the instrument and charged to a potential of 5·0 volts and left connected to the voltmeter. In 38 minutes the potential between the plates of the condenser as measured by the instrument had fallen to 1·0 volts. From this it is calculated that the overall resistance of the thermionic voltmeter *and* condenser due to leakage and grid current was $1 \cdot 7 \times 10^{10}$ ohms. The resistance of the electrometer itself would, of course, be much better than this as there was probably considerable leakage at the surface of the standard condenser.

Uses.

The thermionic voltmeter can be used of course for measuring R.M.S. values of voltage up to very high frequencies as it is effectively screened and bypassed. As an electrometer these types of valve are said to make other electrometers obsolete[3] as they are so convenient, portable and robust. The instrument described above has been successfully used in determining capacity by the method of Faraday.

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STUDIES IN THE CONESSINE SERIES.

Part IV. Action of Nitric Acid on Conessine and the Reduction of One of its Two Isomeric Mono-Nitro Derivatives to Mono-oxy and *Iso*-dioxy-Conessine.

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Several methods of oxidation have already been tried on consessine, but none has thus far led to any definite conclusions in regard to its constitution. Dioxy-conessine, obtained by Warnecke[1] through oxidation of conessine with iodic acid, was further oxidized with the help of sulphuric acid and chromic acid by Giemsa and Halberkann,[2] but they failed to get any well defined product, apart from dimethyl amine. The non-crystalline amino lactonic acid, $C_{19}H_{32}N.\overset{\overset{C}{\frown}}{CO}\cdot O$ $\underset{COOH}{}$ which they claimed to have obtained, was not sufficiently pure for analysis and had a very discouraging yield. A series of basic oxidation products were also obtained from conessine, after its initial isomerisation,[3] through the action of concentrated sulphuric acid, but these as well have thus far evaded crystallisation into pure products. We therefore considered it desirable to extend this line of investigation by studying the action of $KMnO_4$ and HNO_3 on conessine. Potassium permanganate has not so far yielded any well defined products, but the action of nitric acid has proved of enormous interest and opened up an entirely new line of attack on the conessine molecule. The present paper deals with a detailed study in this direction.

When conessine is dissolved in a mixture of glacial acetic acid and concentrated nitric acid (d. = 1·4) (50: 50 by volume) no change takes place even after keeping the solution at room temperature (mean about 30°C.) for 24 hours. On warming it on the water-bath for about 10 minutes, a crystalline base was obtained from the reaction mixture which melted

[1] *Ber.*, 1886, **19**, 60.
[2] *Arch. Pharm.*, 1918, **256**, 201.
[3] S. Siddiqui, *Proc. Ind. Acad. Sci.*, 1935, 426.

at 173°C. (yield 30%) and proved to be not an oxidation product but a nitro derivative of conessine. Longer heating of the solution or substitution of concentrated nitric acid for its half and half mixture with glacial acetic acid lowered the yield of the nitro-derivative and produced undefinable, reddish brown, water soluble products which appeared to be acidic in character. Addition of conessine in small portions to fuming nitric acid with stirring and ice cooling increased the yield of nitro-conessine to 55%. This yield was further improved to 70% of theory by slowly adding 2 parts by volume of fuming nitric acid to a well cooled solution of 1 part conessine in 2 parts of concentrated nitric acid (d. = 1·4), with ice cooling and stirring. On using half the quantity of fuming nitric acid in the last experiment and with more efficient cooling in a freezing mixture, the yield of nitro-conessine was reduced to a minimum but an isomer of it, *iso*-nitro-conessine, melting at 260°C., could be isolated from the reaction product in a 50% yield, apart from 25% of unreacted conessine.

The analytical data and the physical properties of nitro- and *iso*-nitro-conessine leave no doubt as to their being isomeric nitro-derivatives, the isomerism apparently depending on the position of the nitro group on the double bond in conessine. Of the two isomers, nitro-conessine which was obtained first and in a larger yield has been subjected to a more detailed examination. The direct bromination of the bases having resulted in the formation of hydrobromides as noted in the case of *iso*-conessine (S. Siddiqui, *loc. cit.*), the presence of a single double bond in both of them was eventually fixed up through bromination of their metho-bromides and the estimation of bromine in the resulting product.

The reduction of nitro-conessine with stannous chloride and HCl gave instead of an amino-derivative a mono-oxy-product of conessine, $C_{24}H_{40}N_2O$. The same product was obtained on reduction with Zn (equivalent to 12H) and hydrochloric acid, but minute quantities of a dioxy-derivative could also be isolated in this case, which we have provisionally named as '*iso*-dioxy-conessine' to differentiate it from the dioxy-conessine of Warnecke. The action of nitric acid on conessine has thus indirectly led to its oxidation. Both the oxy-derivatives and their salts are well defined, crystalline products and contain the same number of N-methyl groups as conessine. The presence of a double bond in the mono and dioxy products could not be definitely fixed up yet, but from their behaviour towards bromine it appears likely that the original double bond of conessine is present in mono-oxy-conessine but is removed in the dioxy-derivative.

The apparently abnormal behaviour of the nitro-group on reduction is not surprising as nitro-groups situated on double bonds are known to

yield only rarely the corresponding amines on reduction with Zn and HCl or other reducing agents. On the contrary, the nitrogen is very often thereby removed as ammonia, and an oxy-, keto- or a carboxyl takes the place of the nitro-group.[4] In this particular case, however, it has also been possible to reduce the nitro-derivative to the corresponding amine, through its catalytic reduction with Pt black. The description of the amino-base has not been included in this paper, as it is intended to deal with it later after its full characterisation.

The function of oxygen in the two oxy-derivatives of conessine, discussed above, could not thus far be established. The mono-oxy product failed to give an acetyl or benzoyl derivative or a phenyl hydrazone by usual methods, and *iso*-dioxy-conessine was not sufficient in quantity for a detailed study. This and other problems arising out of the present investigations are being studied further and will be dealt with in a subsequent communication.

Experimental.

Nitro-conessine ($C_{24}H_{39}N_2 \cdot NO_2$).—10 c.c. of well cooled fuming nitric acid were added slowly to 5 g. of conessine dissolved in 10 c.c. of concentrated nitric acid (d. = 1·4) with efficient cooling and stirring. The light yellow solution was well diluted with ice and made alkaline with NaOH. The white granular precipitate was filtered, well washed with water and dried. The crude nitro-base thus obtained was crystallised from acetone when it melted at 168°C. (yield 3·5 g.). After a few crystallisations from the same medium it finally melted at 173°C.

Nitro-conessine (m.p. 173°C) is sparingly soluble in ether and petroleum ether, fairly soluble in hot methanol and ethyl acetate and exceedingly soluble in chloroform. It crystallises from ethylacetate and petrol ether in colouriess, elongated prisms [Plate II(*a*)] and from methanol in hexagonal prismatic plates [Plate II(*b*)]. In 1% absolute alcoholic solution it showed $\alpha_D^{36\cdot5^\circ} = +11\cdot0^\circ$. (After drying at 100°C. *in vacuo* over P_2O_5, it gave C, 72·0, 72·0; H, 10·1, 9·7; N, 10·8, 10·6; $-CH_3$, 11·2 per cent., M.W. cryoscopic in benzene, 420; $C_{24}H_{39}N_3O_2$ requires C, 71·8; H, 9·7; N, 10·5; $-CH_3$ for 3 N–CH_3, 11·2 per cent., M.W. 401).

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[4] Nitro-cumarone → ortho-oxy-phenyl acetic acid, Stoermer and Kahlert, B., 1902, **35**, 1640.

Nitro-phellandrene → Carvo-tan-acetone ; Nitroanethol → Anisyl acetone ; Nitro-inden → hydrindon, Wallach, A., 1904, **332**, 323 ; 1904, **336**, 1, 32.

Nitro-uracil → oxyuracil , Behrend and Roosen, A., 1889, **251**, 235.

Nitro-cholesten → cholestanone, Windaus, B., 1920, **53**, 491, 492.

Nitro-conessine-hydrochloride was prepared by bringing together the components in ethereal solution. It was fairly soluble in water, alcohol, and methanol in the hot, less so in the cold and crystallises from water in colourless, scattered, prismatic rods, m.p. 253° C. (decomp.). [Found after drying to constant weight at 100° C. *in vacuo* over P_2O_5: Cl, 15·4; $C_{29}H_{39}N_3O_2 \cdot 2\,HCl$ requires Cl, 15·0 per cent.]

Nitro-conessine-hydroiodide was obtained by adding a concentrated solution of potassium iodide to a solution of the base in dilute acetic acid in bundles of short, stout, colourless, prismatic rods which after recrystallisation from water melted at 252° C. (decomp.).

Nitro-conessine-hydrobromide was obtained in a similar manner as the hydroiodide as short, colourless needles, readily soluble in water or alcohol, m.p. 258° C. (decomp.) after darkening at 246° C.

Nitro-conessine-chloroplatinate was obtained by adding a 4% solution of platinic chloride to an aqueous solution of the hydrochloride, in orange-coloured, flower-like aggregates of prisms, which began to darken at 260° C. and melted with decomposition at 267° C. [Found after drying at 120° C.: C, 35·95; H, 5·05; N, 5·04; Pt, 24·29; $C_{24}H_{39}N_3O_2 \cdot H_2PtCl_6$ requires C, 35·50; H, 4·80; N, 5·17; Pt, 24·06 per cent.]

Nitro-conessine-aurate.—Prepared in the same manner as the chloroplatinate, it formed a golden yellow crystalline powder which reddened at 160° C. and slowly melted 167° C. onwards.

Nitro-conessine-picrate was obtained from the components in ethereal solution as a yellow, crystalline powder, which was sparingly soluble in water, alcohol or methanol, fairly soluble in acetone and melted at 216° C. to a dark red liquid.

Nitro-conessine-dimethoiodide was obtained on adding a chloroform solution of methyl iodide (2·5 mols.) to a chloroform solution of the nitro-base (1 mol.) as an oil, which crystallised on rubbing. On recrystallisation from a mixture of alcohol, acetone and ether, it formed bunches of long, slender needles, readily soluble in methanol or water and melting at 238° C. (decomp.). [Found after drying at 50° C. *in vacuo* over P_2O_5: $-CH_3$, 10·9; $C_{24}H_{39}N_3O_2 \cdot 2\,CH_3I$ requires CH_3 for 5 NCH_3, 10·9 per cent.]

Nitro-conessine-dimethobromide.—Prepared like the dimethoiodide, it formed a hygroscopic crystalline powder which darkened from 215° C. onwards and melted at 237° C. (decomp.).

Bromination.—0·1124 g. of the base was titrated with bromine in chloroform solution with ice cooling. The titration was followed with starch-KI paper. The end point was achieved when 0·0550 g. of bromine

had been added (required for one double bond 0·0467). The oily precipitate thereby obtained was repeatedly washed with ether and evacuated when it turned into a yellow powder (0·144 g.), which began to darken at 176° C. and melted at 233° (decomp.). On admixture with a pure sample of the hydrobromide of the nitro-base, there was no depression in its melting point, and it yielded a halogen-free base which was not sufficient in quantity for purification and analysis but definitely appeared to be nitro-conessine from the behaviour of its m.p. and the mixed melting point.

0·1404 g. of nitro-conessine-dimethobromide was dissolved in glacial acetic acid and 0·0414 g. bromine in the same solvent was added (one double bond required 0·0407 g. of bromine) with cooling. The yellow precipitate obtained after keeping the mixture in cold for a few hours, was washed with ether. It darkend at 192°C., began to froth at 235° C. and melted down at 260° C. [Found in air-dried sample : Br, 42·4 ; $C_{24}H_{30}N_3O_2 \cdot 2CH_3Br \cdot Br_2$ requires Br, 42·6 per cent.]

Reduction of Nitro-Conessine with Zinc dust and HCl.

3·1 g. nitro-conessine (m.p. 168–69°) was dissolved in 35 c.c. HCl concentrated and reduced with 3 g. of Zn dust (equivalent to 12 H). After the reduction was complete, the colourless solution was made strongly alkaline with caustic soda. The white precipitate was filtered, dissolved in dilute acetic acid and treated with KI, whereby a water-soluble and a water-insoluble iodide fraction were obtained. The latter yielded 0·9 g. of an ethyl acetate soluble base, melting at 198–99° C. The water soluble iodide fraction gave 0·1 g. of an ethyl acetate insoluble base, m.p. 274° C. and 0·2 g. more of the ethylacetate soluble base, major fraction of which had been obtained from the insoluble iodide (total yield 1·1 g. 35·5% of theory).

Mono-oxy-conessine ($C_{24}H_{40}N_2O$).—The lower melting base from above was repeatedly crystallised from ethylacetate when it was finally obtained in bundles or a network of colourless needles [Plate II(*c*)], melting at 202–3°. It was insoluble in petroleum ether but soluble in ether or ethylacetate. In 1% chloroform solution it gave $\alpha_D^{30°} = +11°·5$. [Found after drying to constant weight at 100° C. *in vacuo*, over P_2O_5 : C, 77·1, 77·3 ; H, 11·2, 10·9 ; N, 7·5, 7·6 ; CH_3, 12·3 ; $C_{24}H_{40}N_2O$ requires C, 77·4 ; H, 10·8 ; N, 7·5 ; CH_3 for $3N \cdot CH_3$, 12·1 per cent.]

Mono-oxy-conessine-hydrochloride was obtained from the components in ethereal solution in long, colourless, tapering needles which were readily soluble in methanol or water, sintered at 150° C. and melted with decomposition at 273–75° C. [Found after drying to constant weight at 100° C. *in vacuo* : Cl, 16·4 ; $C_{24}H_{40}N_2O \cdot 2HCl$ requires Cl, 16·0 per cent.]

Mono-oxy-conessine-hydroiodide was obtained by adding a concentrated solution of potassium iodide to an acetic acid solution of the base. It crystallised from water in colourless, prismatic rods, soluble in hot alcohol or methanol, and melted at 352° C. (decomp.).

Mono-oxy-conessine-hydrobromide was obtained in the same manner as the hydrochloride in colourless, prismatic rods which were readily soluble in water or alcohol and melted above 360° C. with decomposition.

Mono-oxy-conessine-chloroplatinate was obtained by adding a 5% aqueous solution of platinic chloride to an aqueous solution of the hydrochloride in short, stout, orange coloured prismatic rods, which began to darken at 278° C. and frothed up suddenly at 297° C. [Found after drying at 120° C.: Pt, 24·9; $C_{24}H_{40}N_2O \cdot H_2PtCl_6$ requires Pt, 25·0 per cent.]

Mono-oxy-conessine-picrate was obtained by adding ethereal picric acid to an ethereal solution of the base. It crystallised from methanol in bunches and stars of short, yellow, tapering, prismatic rods, which shrink and darken at 204° C. and melt with decomposition at 249° C. It is sparingly soluble in water, alcohol or methanol.

Mono-oxy-conessine-dimethoiodide was obtained from the components in chloroform solution as an oil which crystallised on rubbing and melted at 298–300° C. (decomp.). [Found after drying at 100° C. *in vacuo*: CH_3, 11·2; $C_{24}H_{40}N_2O \cdot 2CH_3I$ requires for 5 N·CH_3, 11·4 per cent.]

Mono-oxy-conessine-dimethobromide.—Prepared like the dimethoiodide, it formed a colourless, crystalline, hygroscopic powder, melting at 308° C. (decomp.).

Iso-*dioxy-conessine* ($C_{24}H_{42}N_2O_2$).

The ethylacetate insoluble, higher melting base (274° C.), obtained from the water-soluble iodide fraction of the reduction product from nitro-conessine, gave after repeated crystallisations from alcohol pure *iso*-dioxy-conessine, melting at 279–80° C. In 0·25% chloroform solution it gave $\alpha_D^{34°} = -11·0$. [Found after drying to constant weight at 100° *in vacuo* over P_2O_5: C, 73·8, 73·9; H, 10·5, 10·4; N, 7·3, 7·4; CH_3, 11·5; $C_{24}H_{42}N_2O_2$ requires C, 73·8; H, 10·8; N, 7·2; CH_3 for 3 N·CH_3, 11·5; $C_{24}H_{40}N_2O_2$ requires C, 74·2; H, 10·3; N, 7·2; CH_3 for 3 N methyls, 11·6 per cent.]

Iso-*dioxy-conessine-hydrochloride* was prepared by adding ether to a solution of the base in alcoholic HCl, when it came out in clusters of colourless, prismatic rods which blacken from 320° C. onwards and melt above 360° C. [Found after drying to constant weight at 100° C. *in vacuo* over P_2O_5: Cl, 15·4; $C_{24}H_{42}N_2O_2 \cdot 2$ HCl requires Cl, 15·3 per cent.]

Iso-*dioxy-conessine-chloroplatinate* was obtained on adding platinic chloride solution to an aqueous solution of the hydrochloride in long, orange coloured

needles, sparingly soluble in hot water. It began to darken at 270° C. and melted with decomposition at 288° C. [Found after drying to constant weight at 100° C. *in vacuo*, over P_2O_5: Pt, 24·6; $C_{24}H_{42}N_2O_2 \cdot H_2PtCl_6$ requires Pt, 24·3 per cent.]

Iso-*nitro-conessine* ($C_{24}H_{39}N_2 \cdot NO_2$).

3 c.c. well cooled fuming nitric acid was added drop by drop to a solution of 3 g. conessine in 16 c.c. concentrated nitric acid (d. = 1·4) with constant stirring and cooling in a freezing mixture. The pale yellow solution was stirred well for about a minute after addition of the acid and then diluted with ice and made alkaline with NaOH. The flocculent, white precipitate was extracted with ether and the ethereal solution well washed with water and dried over sodium sulphate. The residue left on removal of the solvent was successively exhausted with petroleum ether and acetone. The final residue (0·75 g.) was a white crystalline product, melting at 240° C. The petroleum ether and acetone extracts yielded on concentration 0·5 g. and 0·25 g. respectively of a base melting at 248° C., and the combined mother-liquors of both yielded 0·7 g. of unreacted conessine. The crude base melting at 240° C. and 248° C. (total 1·5 g.), obtained above, was repeatedly crystallised from alcohol, when it finally yielded pure *iso*-nitro-conessine in hexagonal prismatic plates melting at 259–60° C. (nitro-conessine m.p. 173° C), and minute quantities of nitro-conessine through fractionation of the mother-liquors. *Iso*-nitro-conessine is very sparingly soluble in petroleum ether, acetone or ethylacetate but fairly soluble in hot alcohol or chloroform. In 1% chloroform solution it showed $\alpha_D^{30°} = -45°{\cdot}5$ as against $\alpha_D^{36·5°} = +11°{\cdot}0$ noted for nitro-conessine. [Found: C, 71·9, 71·5; H, 10·5, 10·3; N, 10·5, 10·3; $\cdot CH_3$, 11·1; $C_{24}H_{39}N_3O_2$ requires C, 71·8, H, 9·7; N, 10·5; CH_3 for 3 N·CH_3, 11·2 per cent.] No loss of weight was noted on drying the air-dried sample at 100° C. *in vacuo*.

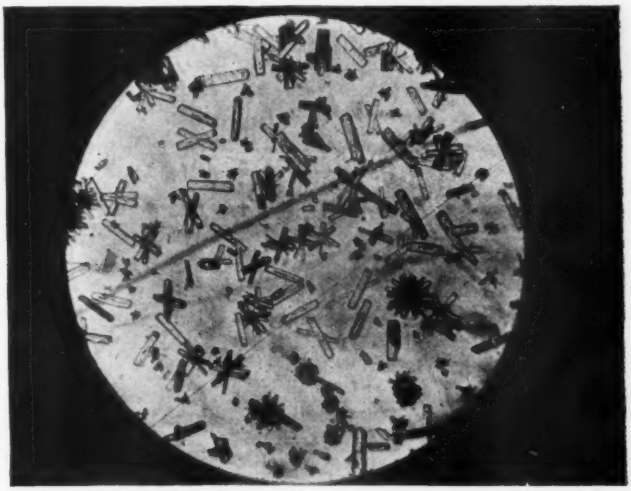
Iso-*nitro-conessine-hydrochloride* was obtained on adding ethereal HCl to an alcoholic solution of the base as an oily product which crystallised on rubbing. It was readily soluble in alcohol, less so in acetone and crystallised with one molecule of water from a mixture of alcohol, acetone and ether, m.p. 239–40° C. (decomp.). On drying the air-dried sample to constant weight at 120° C., it lost 4·0 per cent. of its weight; $C_{24}H_{39}N_3O_2 \cdot 2\ HCl, H_2O$ requires H_2O, 3·7 per cent. [Found in dehydrated salt: Cl, 15·0; $C_{24}H_{39}N_3O_2 \cdot 2\ HCl$ requires Cl, 15·0 per cent.]

Iso-*nitro-conessine-hydroiodide* was prepared by adding a concentrated solution of potassium iodide to a solution of the base in dilute acetic acid. It was soluble in hot water or alcohol and crystallised on cooling its concentrated aqueous solution in long, colourless, tapering needles, melting at 295° C. (decomp.).

Iso-*nitro-conessine-chloroplatinate* was obtained by adding aqueous platinic chloride to an aqueous solution of the hydrochloride, in orange coloured prismatic rods, which darkened at 233° C. and melted with decomposition at 237° C. [Found after drying to constant weight at 130°: Pt, 23·8; $C_{24}H_{39}N_3O_2 \cdot H_2PtCl_6$ requires Pt, 24·0 per cent.]

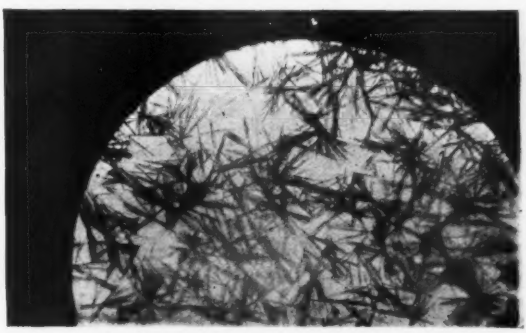
Iso-*nitro-conessine-dimethobromide* was obtained from the components in chloroform solution. It crystallised from alcohol in bunches and stars of stout, colourless needles, m.p. 301° C. (decomp.). [Found after drying at 100° *in vacuo*: CH_3, 12·7; Br, 28·1; $C_{24}H_{39}N_3O_2 \cdot 2\ CH_3Br$ requires for 5 N methyls CH_3, 12·7; Br, 27·1 per cent.]

Bromination.—To 0·0475 g. of the methobromide in glacial acetic acid was added a glacial acetic acid solution of bromine, calculated for one double bond. The mixture was kept overnight and the yellow precipitate was filtered and washed with ether, when it finally yielded a yellowish powder melting at 108–12° C. On treatment with two double bonds equivalent of bromine in a similar manner, the methobromide gave the same product. [Found after drying at 50° C. *in vacuo*: Br, 43·7; $C_{23}H_{39}N_3O_2 \cdot 2\ CH_3Br \cdot Br_2$ requires Br, 42·6 per cent.]



(*a*) Nitro-conessine from Petrol ether.

(*b*) Nitro-conessine from Methanol.



(*c*) Oxy-conessine from Ethylacetate.

ON THE EMISSION AND ABSORPTION BAND SPECTRA OF SELENIUM.

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Introduction.

The spectrum of a discharge through selenium vapour was measured by Messerschmitt[1] in 1907, who found that it consists of a large number of bands in the near ultra-violet and visible regions between λλ 3707 and 5881. In recent years, Rosen[2] obtained the bands of selenium vapour in absorption and was the first to propose a vibrational quantum analysis for them, which shows definitely that they are due to the diatomic molecule Se_2. All the bands observed in absorption were included in one electronic system for which the following equation was deduced :

$$\nu = 27307 + (247 \cdot 2\, v' - 2 \cdot 3\, v'^2) - (397 \cdot 5\, v'' - 1 \cdot 32\, v''^2). \quad (1)$$

Nevin,[3] in a short note to *Nature*, confirmed in the main this analysis of Rosen but in addition found that the emission bands at longer wave-lengths which were not observed by the latter in absorption, could be arranged into two systems which arise in two different excited levels but have a common final state which is the same as the ground level of the molecule as found in absorption. According to him the spectrum therefore consists of three band-systems, the α-main system observed in emission and absorption, the β-diffuse blue emission bands and the γ-green-yellow emission bands. The following equations (in which $u = v + \frac{1}{2}$) are derived by Nevin for these three systems :

$$\alpha\text{-System} : \nu = 27371 + (254 \cdot 7\, u' - 2 \cdot 42\, u'^2) - (387 \cdot 8\, u'' - 0 \cdot 63\, u''^2) \quad (2)$$

$$\beta\text{-System} : \nu = 21945 + (431 \cdot 1\, u' - 0 \cdot 83\, u'^2) - (373 \cdot 5\, u'' - 0 \cdot 66\, u''^2) \quad (3)$$

$$\gamma\text{-System} : \nu = 18342 + (336 \cdot 3\, u' - 0 \cdot 19\, u'^2) - (386 \cdot 5\, u'' - 0 \cdot 59\, u''^2) \quad (4)$$

Many of the bands of the α-system are also known in fluorescence. Isotopic effect has been observed by Olsson[4] for some of the bands of this system. This necessitated a revision of the v' numbering and accordingly Olsson corrected equation (2) to

$$\nu = 26010 + (287 \cdot 7\, u' - 2 \cdot 42\, u'^2) - (387 \cdot 8\, u'' - 0 \cdot 63\, u''^2). \quad (5)$$

In a more recent paper Nevin[5] has confirmed the isotopic effect and has proposed the following slightly different equation to represent the bands of the α-system :

$$\nu = 26083 + (265 \cdot 1\, u' - 1 \cdot 878\, u'^2) - (381 \cdot 6\, u'' - 0 \cdot 144\, u''^2 + 0 \cdot 0088\, u''^3). \quad (6)$$

Moraczewska[6] added two more absorption band-systems in the ultra-violet so that till very recently the spectrum of Se_2 was analysed into five systems all of them having different excited states but a common final state.

Jevons[7] has summarised these results in his ' Report ' from which the following term scheme is prepared, the position of B level being changed in view of the isotopic effect observed.

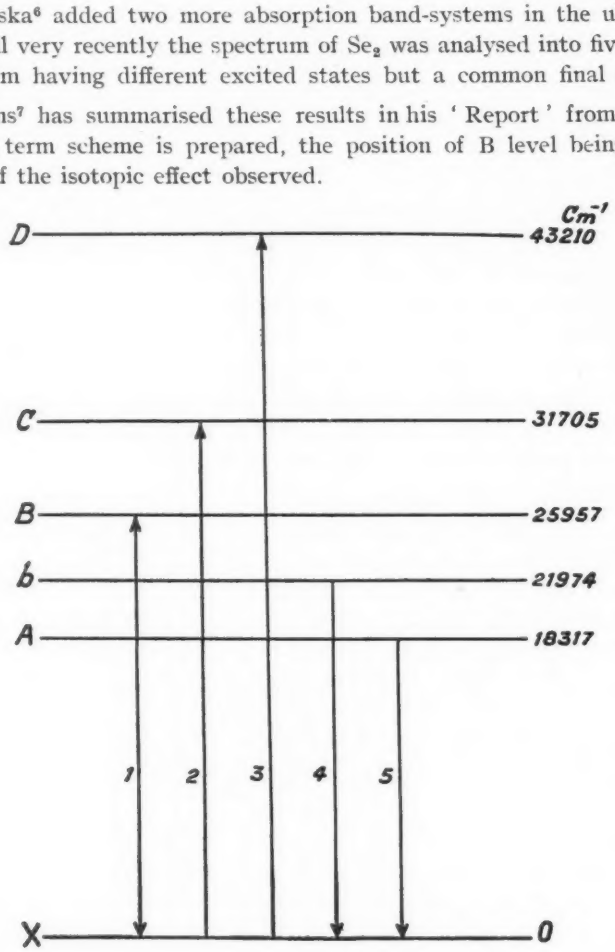

FIG. 1.

1. α-Main band-system in absorption, fluorescence and emission.
2 & 3. Weak absorption bands of Moraczewska.
4. β-diffuse blue emission bands of Nevin.
5. γ-green-yellow emission bands of Nevin.

In a series of papers, Rosen and Desirant[8] and Rosen and Monfort,[9] report a re-investigation of the emission spectrum of selenium vapour. In addition to α-system they find that the various bands observed by them can be classified into four more systems, three of which have their final state in common with the ground state of the molecule and the fourth has its initial state in common with the α-system but has a different final state so that according to them the term scheme of the molecule is given by the diagram of Fig. 2. The system of fluctuations, 6 of Fig. 2, is the same as the γ-green yellow system of Nevin but with a different analysis.

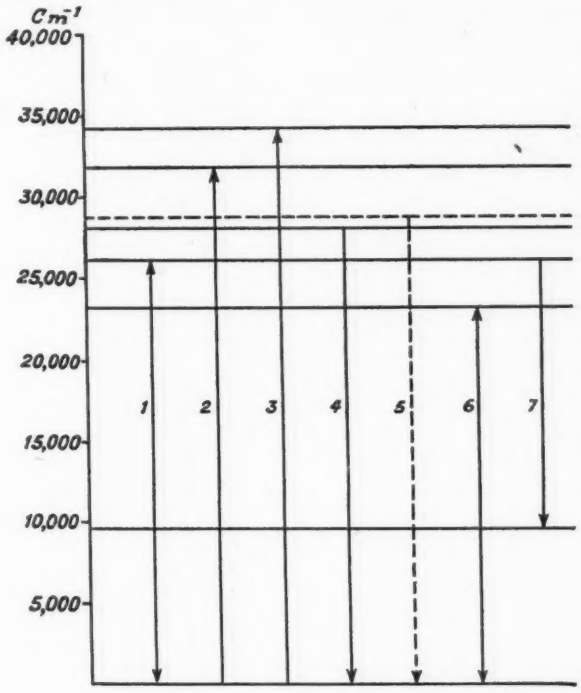

FIG. 2.

1. α-Main band-system.
2 & 3. Absorption bands of Moraczewska.
4 & 5. Bands of Rosen and Desirant.
6. System of fluctuations (same as system 5, Fig. 1 but with a different analysis).
7. Bands of Rosen and Monfort.

In analogy with the homologous molecules O_2 and S_2 the ground level of the molecule was assumed to be $^3\Sigma$ and the transition involved in the

α-main band-system to be $^3\Sigma - {}^3\Sigma$. Olsson,[4] however, has proposed a rotational analysis for some of the bands evidently belonging to this system, which shows that the transition involved is $^1\Sigma - {}^1\Sigma$. If the character of the levels B and X is $^1\Sigma$, considerable difficulty is encountered for correlating the molecular terms with the terms of separated atoms and consequently for deriving the energy of dissociation of Se_2 in its unexcited ground state. We shall discuss this later.

Another peculiarity of this system is that the spacings of the vibrational levels both in the initial and in final states are very irregular so that none of the equations (1), (2) and (5) represents the bands with the desired accuracy. Rosen and Desirant[8] have deduced the following equation which they develop from the five bands measured by Olsson[4] under high dispersion and with greater accuracy :

$$\nu = 25957 + (277 \cdot 8\, v' - 2 \cdot 25\, v'^2) - (391 \cdot 5\, v'' - 1 \cdot 06\, v''^2). \qquad (7)$$

This equation also fails to represent the bands satisfactorily. That the irregular spacing of the vibrational levels observed is not due to the inaccuracies in measurement is clear from the work of Nevin who has measured the whole system in absorption under high dispersion and derives equation (6). By an application of this equation he has been able to show that pronounced perturbations occur in certain levels of the excited state. The cubic term which is found necessary to represent the final vibrational function is quite indicative of the fact that the observed spacings of the vibrational levels of the final state are much more irregular than those of the initial state. In view of this state of our knowledge regarding the spectrum of Se_2, it was thought desirable to study it both in emission and absorption.

Emission Spectrum.

The spectrum was produced by an uncondensed discharge through selenium vapour in the presence of argon. For this purpose an H-type discharge tube having aluminium electrodes and the usual side bulbs containing P_2O_5 and selenium, was used. This discharge tube had a quartz window fitted on to it and was run on a $\frac{1}{4}$ kilowatt transformer. The side bulb containing selenium was fixed vertically to the middle of the horizontal part of the discharge tube. The bulb was heated until some of the selenium melted and flowed down to the horizontal part of the discharge tube. In order to get an intense spectrum, which was viewed end on, it was necessary to keep this selenium in the molten condition. The presence of argon facilitated the discharge but did not seem to play any other rôle. Commercial argon which contained slight impurities of nitrogen and

oxygen, was completely purified before use, by allowing it to stand over heated calcium and magnesium turnings. The discharge obtained was of a brilliant blue colour. The spectrum was photographed on a three-prism glass spectrograph having a dispersion of 6 Å/mm. at 4000 Å.U. of about 14 Å/mm. at 5000 Å.U. and of about 26·5 Å/mm. at 5800 Å.U. A medium Hilger quartz-spectrograph was also used to investigate the spectrum in the ultra-violet. The dispersion of this instrument is rather low but since the glass spectrograph used could photograph the spectrum above 3800 Å.U. and since there are only a few bands below this region in the ultra-violet, for which more accurate data are available, no attempt was made to photograph them under higher dispersion. The last band registered on the plate however had a wave-length of λ 3451·6. Copper arc lines as well as lines of helium and mercury in some cases, were utilised as standards. The plates were measured on an Abbe comparator. The accepted values of wave-lengths of the bands represent the mean of three measurements. For bands which are well defined these values did not differ among themselves by more than 0·2 Å.U. The agreement has not been so good for a large number of diffuse bands, which, in general, showed a discrepancy of not more than 0·5 Å.U. among the three measurements. Table I contains the list of observed bands together with their visually estimated intensity and their classification as proposed in this paper. Fig. 3 is an enlarged spectrum of the bands and Fig. 4 shows the microphotograms of the bands. The spectrum did not show any bands in the near infra-red, the region investigated being up to 8500 Å.U.

The bands extend from λ 3800 to λ 5875 and are all degraded towards the longer waves. Except for one solitary band which happens to be the (0, 0) band of the β-system reported by Nevin no band degraded towards the shorter waves has been observed. Starting from the short-wave side bands are quite sharp up to about λ 4000. From λ 4000 to λ 4900 the bands are diffuse and are in addition masked by an overlapping continuum. From λ 4900 to λ 5400 the bands are still diffuse but they occur in definite groups and the overlapping continuum is much weaker. Above λ 5400 the bands are particularly sharp and appear also in definite groups. The reproduced microphotometer plates exhibit these peculiarities clearly. From λ 4800 upwards the appearance of the bands in distinct groups conveys, especially from the photometer records, a peculiar fluctuation of intensity. Such an intensity fluctuation, however, need not be emphasised and is by no means uncommon in band systems where bands belonging to different transition and having different intensities happen, by chance, to lie near together

as if in a sequence. To a certain extent the main band-system of sulphur exhibits a similar behaviour of intensity fluctuation.

Analysis.

At the outset we should like to draw attention to the very irregular spacing of the vibrational levels, which appears to be a distinctive feature of this spectrum. There seems to be little doubt about the correctness of the already existing analysis of the a-system. In Tables II and III, data for the vibrational differences in both the states have been collected according to Nevin's[5] measurements. Figs. 5 and 6 represent the relation between $\omega(v)$ and v in the initial and final states according to Nevin's values.

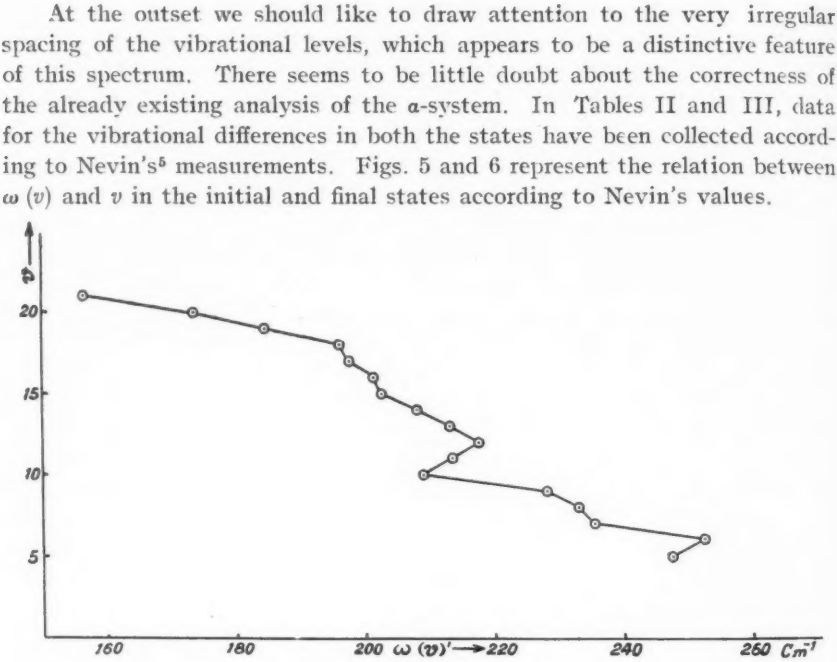

FIG. 5.

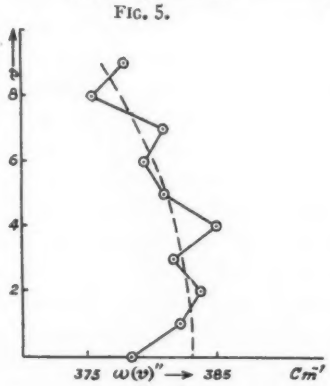

FIG. 6.

It will be seen that the mean vibrational differences both in the initial and final states are irregular in the extreme and even for the same vibrational

difference which is obtained as the mean of many observations, the individual values differ very widely among themselves. It is clear that perturbations of an extensive nature occur. Nevin has drawn attention to this fact and shows that very pronounced perturbations occur in the levels $v' = 7$ to $v' = 11$. Bands having v' values in this range comprise practically 75% of the total number of bands observed in absorption. How far the irregularities and discrepancies observed in the final state are entirely due to these perturbations in the excited state is uncertain but it is possible that perturbations may be present even in the lower state itself brought about by the intersections of at least two potential curves namely of the $^1\Sigma$ and $^3\Sigma$ states both of which arise out of Se ^3P + Se ^3P. For an analysis of the emission spectrum where we get a large number of bands, a recognition of the existence of perturbations is to our mind important. It is possible to pick out a few bands which show a greater regularity of spacing and many such analyses have been tried by us, but in all cases they comprise only a small number of the total bands and show no interrelation among themselves.

We believe therefore that a correct interpretation of the bands does not lie this way and the very complicated nature of bands mars the simplicity of vibrational structure common to band-systems of a less extensive nature. Evidently, unless data of rotational analysis are obtained and the origins of the bands determined, expressions for the vibrational functions will be very approximate.

The microphotographs Fig. 4, first suggested the possibility that the bands forming successive groups might belong to successive sequences. If we take the very distinct groups starting from λ 5458, it is indeed possible to arrange the three groups F, G and H into three successive sequences, as has been done by Nevin. These bands form part of the β-yellow green system of Nevin or the so-called system of fluctuations of Rosen and Monfort. Bands above λ 5400 when arranged according to this scheme yield vibrational differences for the final state, which are very close to the vibrational differences of the ground state. But since an extension of this analysis to the similar groups of bands at shorter wave-lengths was not satisfactory an attempt was made to arrange them in a slightly different way with a view to see if the analysis gave for the initial vibrational differences, values corresponding to those of the main band-system. If instead of taking successive bands, we arrange alternate bands (the best example is group G) as forming a sequence, it is found that the initial vibrational differences roughly correspond with those of the main band-system, while

the final vibrational differences were of an order of magnitude which could be expected for high v'' values of the final vibrational term of the main band-system indicating that these bands belong to the α main band-system and do not form a new system. Extending this method to the group of bands on the shorter waves it was possible to arrange them in the same scheme. In most of these groups, however, it was found that the regularity of the alternate bands forming sequences was in many cases disturbed, till at last when we come to the group at λ 4800, the bands are completely confused. Between $\lambda\lambda$ 4800 and 4000 the bands possess no apparent regularity and present more or less a very chaotic distribution resembling that of the bands of a multi-atomic molecule. The procedure for the analysis proposed here has therefore been the following. The bands of the α-system were first placed in their proper positions in the table, the v' v'' numbering being the same as that given by Nevin and other workers. The groups F, G and H were then analysed and their v' numbering fixed as indicated by the rough correspondence of the initial differences of these bands with those of the main system. The gulf between the two sets of bands in the table was then bridged by arranging the successive groups of bands between $\lambda\lambda$ 5400 and 4900. The bands between $\lambda\lambda$ 4900 and 4000 being diffuse and more complicated offer the greatest difficulty and uncertainty for the analysis. A few bands could not be fitted into the scheme. These are given in Table IV. They are mostly diffuse and are probably only structure lines.

The analysis is displayed in Table V. The vibrational differences in the two states of this system as deduced from the analysis proposed here are given in Tables VI and VII. On account of the very irregular nature of the spacing we do not propose to derive the usual vibrational equation. The relation between ω (v) and v for the two states is shown in Figs. 7 and 8. Successive points are joined by continuous lines while the dotted curves probably represent the true relation between ω (v) and v in the absence of perturbations. As is well known this relation is in most cases not linear. The general form of the curve is such that for low values of v it has a negative curvature (concave to both axes) which after a point of inflexion changes into a positive curvature (convex to both axes). The curve for the initial state Fig. 7, appears to conform to such a general form. Except for slight deviations, it starts with a negative curvature. The point of inflexion is, however, at a surprisingly low value of v, *viz.*, 5, after which it shows a positive curvature, the smoothness being destroyed by what are apparently pronounced perturbations between $v = 10$ and 14. The curve for the final state (Fig. 8) is much more complicated. It is possible to draw two curves one with a negative curvature (dotted curve 1) for values of v up to 12 and

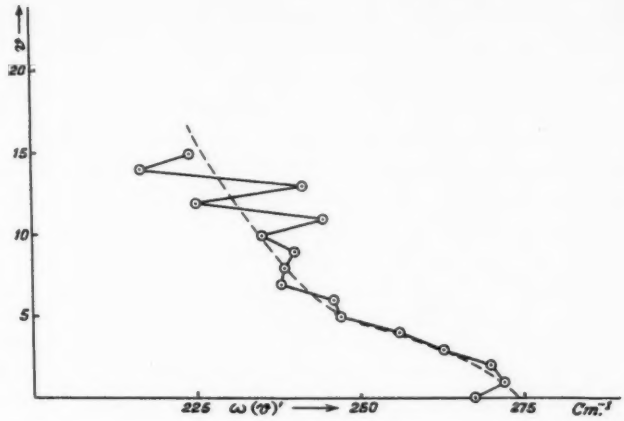

FIG. 7.

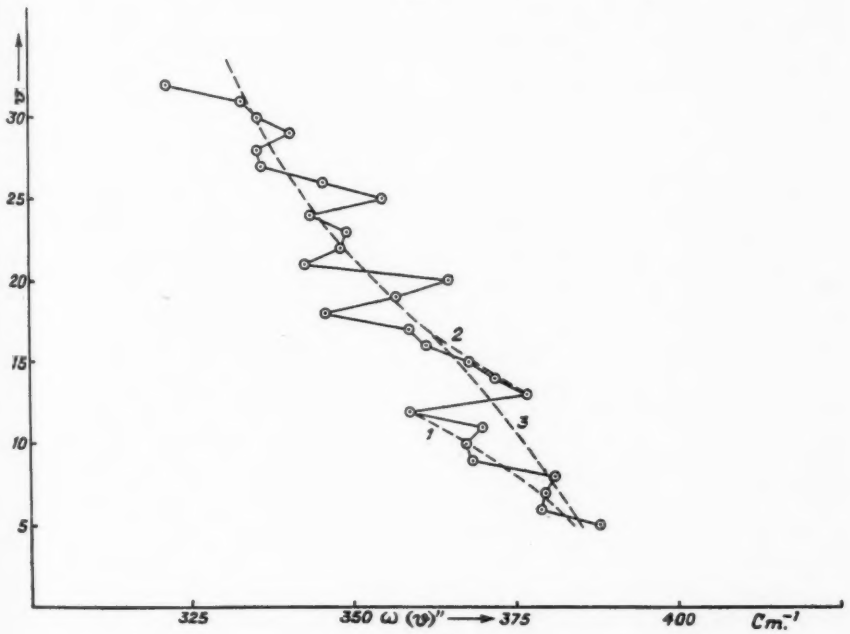

FIG. 8.

another with a positive curvature (dotted curve 2) from $v = 13$ onwards. In each case there are numerous perturbations, those for the curve with positive curvature being more pronounced between $v = 18$ and 20 and

between $v = 25$ and 28. The break between the two curves occurs at the point of inflexion of the dotted curve 3 which probably indicates the general relation between $\omega(v)$ and v for this state.

The analysis proposed here differs in one essential respect from all the others proposed till now. All the bands except those found in absorption by Moraczewska (systems 2 and 3 in Fig. 2) and by Rosen and Monfort in emission (system 7 in Fig. 2) are comprised in one system. The γ-bands of Nevin (system 5 of Fig. 1) or the so-called fluctuation bands of Rosen and Monfort (system 6, Fig. 2) are parts of this system which is analogous to the extensive main band-system of sulphur. The present plates do not record any band degraded towards the short waves except one at λ 4552·3. This is probably the (0, 0) band of the β-diffuse blue emission band-system of Nevin (system 4, Fig. 1). If these bands are due to Se_2 the conditions of excitation appear to be different and since no detailed data regarding the bands are available further work is necessary. The new band-system recorded by Rosen and Monfort (system 7, Fig. 2) has according to them its initial state in common with the main band-system and has a frequency of 325 cm.$^{-1}$ for its lower state. It seemed, at first, possible to include these bands in the analysis proposed here, for the frequency of 325 cm.$^{-1}$ might be regarded as the frequency of vibration of the ground state for high v'' values. But it was found that such an extension was not possible. This therefore constitutes a new system which arises out of a transition from level B at 25957 cm.$^{-1}$ to a level at 9251 cm.$^{-1}$ above the ground level X.

Rosen and Desirant[8] describe another band-system obtained by high frequency discharge through selenium vapour. This they analyse into two systems, 4 and 5 of Fig. 2. The bands lie in the ultra-violet between $\lambda\lambda$ 2970 and 3417. They appear at low temperatures before the α-system develops but when the temperature is raised the α-bands become incomparably more intensified. They attribute these bands to the excitation of the Se_2 group in a polyatomic molecule of selenium and show that some of the bands agree in their wave-lengths approximately with the first set of absorption bands (system 2, Fig. 1) of Moraczewska. We shall show later that it appears probable that these bands are due to SeO_2.

Absorption Spectrum.

The absorption spectrum of selenium vapour has been studied by Rosen,[2] Moraczewska[6] and Nevin.[5] Rosen obtained the bands of the α-main band-system followed by a continuum. The bands however do not go to form a definite convergence limit, the spacing between the last two observed bands being still about 175 cm.$^{-1}$ Nevin has measured these bands under

higher dispersion. Moraczewska found, in addition to this system, two more sets of bands (systems 2 and 3 of Fig. 1) on the shorter wave-length side of α-system. These were obtained at comparatively low temperatures (about 250° C.) and are not found to be followed by continua. Since the vapour of selenium is known to consist mainly of diatomic molecules only at temperatures higher than 900° C., the presence of these bands at low temperatures must mean either that they are not due to the diatomic molecule Se_2 or that the coefficient of absorption of Se_2 vapour is so great that even a very small percentage of diatomic molecules which will be present at this low temperature, is able to exhibit measurable absorption. This possibility is by no means remote because in our experiments the α-bands already appear at a temperature of about 400° C. which means that the coefficient of absorption is already very high in the region of 3300 Å.U. It is known that the coefficient of absorption increases very rapidly with the decreasing wave-length and therefore provided there be any absorption in the further ultra-violet, it will have a very high coefficient. The experiments in absorption were undertaken with the following objects :

(1) To trace the bands of α-system up to their convergence limit ;

(2) To search for similar convergence limits for the two band-systems of Moraczewska ; and

(3) To correlate the convergence limits to dissociation processes and derive the energy of dissociation of the ground level of the molecule.

Absorption cells of different lengths have been used. Two of these were of fused quartz with plane ends and of length 5 and 20 cm. These were kept in electric stoves which were sufficiently long to ensure a uniform temperature throughout the whole length of the absorption cell in each case. The substance was introduced into the cell through the T-piece which was also fused on to the cell. The T-piece was then attached to the vacuum part of the apparatus. Temperatures up to 500° C. were employed. The third absorption cell was a porcelain tube of length 80 cm., which was placed in an electric furnace whose temperature could be regulated up to 1000° C. To the two ends of the porcelain tube protruding out of the furnace, were fixed copper jackets to which quartz windows were cemented. Each of these jackets had a T-piece attached to it so that the absorption tube could be exhausted. The substance was contained in a porcelain boat which was introduced into the absorption tube before one of its ends was fitted with the copper jacket. For each fresh introduction of the substance, evidently the copper jacket had to be taken out and after introducing the substance it had to be again cemented on to the absorption tube. These

jackets were surrounded by copper spirals through which cold water was kept circulating so that the clogging of the quartz windows was prevented. In all cases, a hydrogen tube giving rise to the continuous spectrum was employed as the source of continuous spectrum. Photographs were taken at different temperatures using a medium Hilger quartz-spectrograph as the resolving instrument.

No absorption bands were observed below 300° C. with any of the absorption cells. The absorption bands mentioned by Moraczewska[6] for the production of which low temperature is said to be favourable are absent in all our experiments under varying conditions of tube length, quantity of substance in the tube and temperature. The α-band-system invariably makes its appearance at 400° C. in all the experiments. The intensity of absorption increases with increase in temperature but in no case were we able to extend the stystem to its convergence point. Brown[10] by using a long absorption cell and low temperatures has pushed the absorption bands of iodine almost to the point where $\Delta\,\omega = 0$. We have tried at 400° C. the absorption cell of 80 cm. and with a trace of selenium but have not been able to photograph any band below λ 3239. Fig. 9 is a typical microphotometer curve of the absorption bands and the attendant continuum. It will be seen that though the bands do not go to the convergence point still the breadth of the continuum covers only a range of 23 Å.U. from λ 3223 to λ 3046, or from 3·8 to 4·1 e.v. The maximum of continuous absorption which is not so sharply distinguished is at λ 3168. Probably longer absorption cells are necessary to bring about the required development of the bands. In some of the experiments especially with the porcelain tube, we observed some absorption bands in the region of the first set of Moraczewska's bands ($\lambda\lambda$ 2758–3150) but we soon discovered that this was due to a small leak in the apparatus. This leads us to think that probably the Moraczewska bands are due to an oxide of selenium. The absence of a continuum following the bands, though the region where we expect it (roughly λ 2700) is investigated, further indicates that the bands may not be due to Se_2. Indeed, there is a fairly good coincidence between many of these bands of Moraczewska and those observed directly in the absorption spectrum of SeO_2.[11] This is shown in the following table in which also the wave-lengths of some of the bands of systems 4 and 5 (Fig. 2) of Rosen and Desirant which agree with those of Moraczewska's bands, are included.

TABLE VIII.

Moraczewska bands λ	Rosen and Desirant λ	SeO_2[11] λ
3150	3151	3158·1
3128	3129	
3107	3105	3107·5
3087	3082	3092·0
3064	3066	3070·4
3041	3043	3044·4
3018	3020	3008·9
2998	2999	3007·8
2979	2980	2986·5
2960		2963·6
2941		2950·9
2923		2928·6
2906		2906·6
2888		2884·5
2870		2872·7
2850		2851·4
2832		2831·4
2816		2819·8
2799		2800·6
2787		2788·3
2774		2772·7
2758		2750·3

It is clear that if Moraczewska's bands are due to SeO_2 Rosen and Desirant bands are also due to it. The second set of Moraczewska's bands also are not observed by us in absorption. They lie already in the limiting region of quartz and probably extend to still shorter wave-lengths. We have, however, no remarks to offer on this system.

Discussion.

The absorption and emission spectra of Se_2 therefore consist of two systems as shown in Fig. 10 both of which have a common initial level.

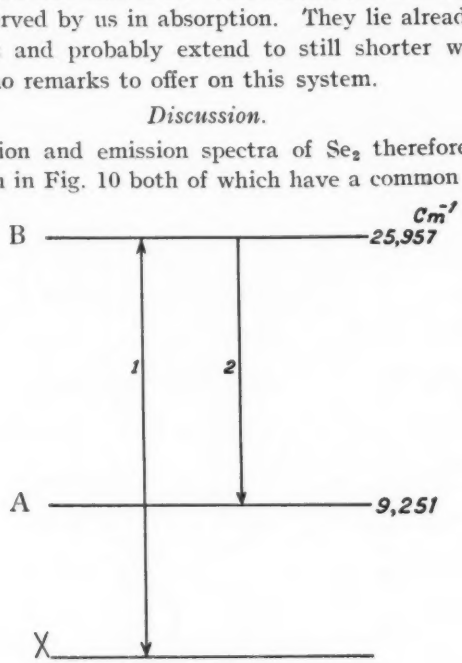

FIG. 10.

1. Absorption and emission main band system.
2. Bands of Rosen and Monfort[9] in emission.

For a correlation of these molecular terms to the terms of the separated atoms it is necessary to know the energies of dissociation of the molecule in the three states. One of the methods of determining this quantity is the extrapolation of the vibrational levels. While this method often leads to too high values, it has been recently shown[12] that under certain conditions this method can be used for such a correlation. One of these conditions is that the vibratioual levels of the two states in question should be known with equal accuracy, so that the relative error in the evaluation of ω and ωx is small. For Se_2 this method is particularly unsuited because of the pronounced irregularities in the spacings of the vibrational levels in the ground state which render uncertain the evaluation of the anharmonic constant. The absorption spectrum on the other hand gives us, from the convergence limit, a very accurate measure of the energy of dissociation

of the molecule in the excited state. In Se_2 the convergence limit, as is pointed out already, is not so clearly defined as in the more favourable example of I_2; but the witdh of the continuum following the bands, covers only a small spectral range between λ 3223 to λ 3046 (*i.e.*, from 3·8 to 4·1 e.v.), the maximum in the continuum being at λ 3168, which gives 31557 cm.$^{-1}$ = 3·9 e.v. If we deduct from this the energy of excitation of the level B, which is 3·2 e.v. corresponding to 25957 cm.$^{-1}$, we obtain for the energy of dissociation for the level B, the value 0·7 ± 0·2 e.v. In order to deduce the energy of dissociation of the ground state from the value of the convergence limit, we must know the character of the two terms B and X. Originally it was assumed that both these terms were of the $^3\Sigma$ type, in analogy with the homologous molecules of O_2 and S_2 for which the character of the terms has been definitely established. But the partial rotational analysis of some of the bands evidently belonging to the α-system, proposed by Olsson[4] indicates that the two levels in question are of $^1\Sigma$ type, the level B being $^1\Sigma_u^+$ and X being $^1\Sigma_g^+$.

Now the possible molecular Σ terms that arise from Se ^{3}P + Se ^{3}P are $^1\Sigma_g^+$, $^1\Sigma_g^+$, $^1\Sigma_u^-$, $^3\Sigma_u^+$, $^3\Sigma_u^+$, and $^3\Sigma_g^-$. If we restrict ourselves to terms of same multiplicity, these cannot combine with one another and therefore whether both the levels are singlets or triplets, they cannot both arise from unexcited atoms. Therefore, as in O_2 and S_2, the excited term B must involve an excited atom. It may be that both atoms are excited, if the analogy with O_2 and S_2 does not hold. On the assumption that the molecular terms are singlets and that the excited term involves only one excited atom of Se, it is clear that such an excitation must lead the Seatom to an excited triplet level so that in combination with Se ^{3}P it can yield a singlet molecular term. Such a level nearest to the ^{3}P ground level of Se, is the $4p^3$ 5*s*, ^{3}S which is 51001 cm.$^{-1}$ above Se $4p^4$ ^{3}P.[13] This leads to a negative value for the energy of dissociation of Se_2 in the ground state and has therefore to be rejected. We must then assume that the excited term is built up of two Se atoms each of which is excited to 4 p^4 ^{1}D which is 9576 cm.$^{-1}$ above 4 p^4 ^{3}P. Deducting twice 9576 cm.$^{-1}$ from 31557 cm.$^{-1}$ we get 12405 cm.$^{-1}$ = 1·5 e.v. as D″ (Se_2). On this basis, the level A will also be $^1\Sigma_g^+$, produced by two unexcited Se atoms.

Rosen and Desirant, by a similar reasoning but by using extrapolated values for D′ (B), obtained D″ (X) = 1·9 e.v. To our mind the value deduced by the absorption experiments is more reliable especially in this case. In any case D″ (X) for Se_2 is unusually too low. From the energies of dissociation of O_2 (5·05 e.v.) and S_2 (3·8 ± 0·2 e.v.) and from considerations

of various results in absorption spectra[14] we expect the energy of dissociation of Se_2 to be between 2·5 and 3·0 e.v. We have shown that such a value is impossible if the singlet character of the levels is established. If the ground level is $^1\Sigma$ Se_2 vapour must be diamagnetic. Recent work* on the measurement of magnetic susceptibility of selenium vapour at high temperatures seems to indicate that this is by no means true and that diatomic selenium is paramagnetic. Detailed investigation is in progress but preliminary results establish this fact beyond doubt. Therefore the ground term of Se_2 is very probably $^3\Sigma$ and its analogy with O_2 and S_2 seems to be complete. The level X then is $^3\Sigma_g^-$ and arises from Se 4 p^4 3 P + Se 4 p^4 3 P. The excited term B is $^3\Sigma_u^-$ and involves an excited Se atom in Se 4 p^4 ^{1}D so that the energy of dissociation D″ X (Se_2) is 31557 − 9576 = 21981 cm.$^{-1}$ = 2·7 ± 0·2 e.v. Now the level A lies at 9251 cm.$^{-1}$ = 1·14 e.v. above the ground level. It appears that the bands which involve this level require special methods of excitation because they have not been observed either by us or by other workers but have been obtained by Rosen and Monfort under high frequency discharge. Quite tentatively we suggest that the level A is a singlet level and forms the analogue of the level A $^1\Sigma_g^+$ in O_2, and that it arises likewise out of unexcited atoms.

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* Private communication from a forthcoming paper by Dr. Lessheim and Mr. Khanna, Lahore.

TABLE I.

Int.	λ-in air	ν-in vac.	v'	v''	Int.	λ-in air	ν-in vac.	v'	v''
3	3815·5	26201	10	6	2	4827·4	20709	7	19
2	3828·1	26115	8	5	0	4836·5	20670	0	14
5	3849·9	25967	9	6	1	4857·2	20582	8	20
2	3872·0	25819	10	7	0	4876·6	20500	15	25
4	3885·9	25727	8	6	0	4883·9	20470	2	16
6	3907·2	25587	9	7	0	4885·3	20464	6	19
*d*3	3921·3	25495	7	6	*db*2	4902·0	20394	3	17
7	3943·5	25351	8	7	*db*0	4910·5	20359	13	24
1	3959·8	25247	6	6	0	4912·1	20352	7	20
8	3980·7	25114	7	7	0	4918·6	20352	4	18
*d*5	4002·9	24975	8	8	0	4925·2	20298	0	15
2	4014·8	24901	11	10	0	4939·7	20239	11	23
2	4019·8	24870	6	7	0	4943·8	20222	5	19
*d*2	4032·9	24789	12	11	0	4948·6	20202	1	16
4	4041·7	24735	7	8	0	4965·7	20133	12	24
3	4049·0	24691	10	10	0	4971·1	20111	6	20
2	4064·4	24597	8	9	1	4993·3	20022	13	25
2	4082·9	24486	6	8	0	4998·5	20000	10	23
2	4088·3	24453	9	10	0	5003·8	19979	4	19
2	4093·6	24422	12	12	0	5017·6	19924	0	16
4	4103·9	24360	7	9	2	5023·6	19901	14	26
4	4148·9	24096	6	9	1	5028·0	19883	11	24
4	4168·6	23982	4	8	*d*2	5032·3	19866	8	22

TABLE I—(*Contd.*).

Int.	λ-in air	ν-in vac.	v'	v''	Int.	λ-in air	ν-in vac.	v'	v''
5	4216·9	23707	9	12	*b*1	5037·0	19848	5	20
7	4255·1	23495	5	10	*b*1	5042·0	19828	1	17
4	4258·0	23479	8	12	0	5052·1	19788	12	25
2	4290·2	23302	12	15	+0	5059·5	19758	9	23
7	4303·0	23233	7	12	1	5112·5	19554	0	17
3	4306·5	23214	4	10	*d*2	5114·4	19547	11	25
1	4389·0	22778	1	9	*d*2	5124·2	19510	8	23
2	4393·5	22755	8	14	3	5131·0	19484	5	21
1	4396·5	22739	5	12	4	5134·3	19471	1	18
1	4405·7	22692	2	10	4	5141·0	19446	15	28
2	4420·2	22617	6	13	5	5144·2	19434	12	26
1	4424·3	22596	3	11	*d*1	5150·7	19409	9	24
2	4438·2	22525	0	9	*d*0	5155·8	19390	6	22
1	4441·8	22507	7	14	+2	5162·4	19365	3	20
1	4445·6	22488	4	12	*d*2	5173·5	19324	16	29
2	4460·9	22411	1	10	*d*1	5180·2	19299	10	25
2	4467·1	22380	5	13	*d*1	5184·3	19284	7	23
1	4478·5	22323	2	11	*d*1	5194·6	19245	4	21
*d*2	4512·4	22155	0	10	*d*1	5205·3	19206	0	18
*d*2	4517·5	22130	4	13	*d*0	5010·1	19188	11	26
*d*3	4534·9	22045	1	11	*d*0	5215·0	19170	8	24
0	4556·2	21942	2	12	*d*2	5225·9	19130	1	19
0	4575·5	21849	3	13	*d*2	5234·0	19101	15	29

TABLE I—(*Contd.*).

Int.	λ-in air	ν-in vac.	v'	v''	Int.	λ-in air	ν-in vac.	v'	v''
*d*4	4586·3	21798	10	18	*d*1	5239·1	19082	12	27
4	4591·8	21772	7	16	*d*2	5245·1	19060	9	25
3	4610·0	21686	1	12	*d*2	5250·7	19040	6	23
0	4616·0	21658	8	17	*d*2	5262·0	18999	3	21
2	4630·2	21591	2	13	*d*3	5266·7	18982	16	30
0	4639·6	21548	9	18	*d*1	5271·3	18965	13	28
2	4641·8	21537	6	16	*d*0	5280·9	18931	7	24
1	4653·4	21484	3	14	*d*1	5292·7	18889	14	29
1	4657·9	21417	0	12	*d*1	5303·7	18850	11	27
0	4673·5	21391	4	15	*d*0	5309·3	18830	8	25
1	4689·3	21319	1	13	*db*2	5318·2	18798	5	23
0	4713·3	21211	2	14	*d*0	5321·7	18786	1	20
1	4719·3	21184	6	17	*d*2	5329·9	18757	15	30
1	4747·2	21059	7	18	*d*1	5332·3	18748	12	28
0	4750·1	21046	0	13	*d*0	5338·5	18727	2	21
0	4754·0	21029	4	16	*d*2	5342·7	18712	9	26
0	4771·1	20594	14	23	*d*2	5350·5	18685	6	24
0	4776·0	20932	1	14	0	5358·7	18656	3	22
3	4794·3	20852	12	22	2	5381·2	18578	7	25
0	4803·5	20812	6	18	+4	5388·3	18554	4	23
*d*4	4819·6	20743	3	16	1	5393·4	18536	14	30
4	5400·9	18510	11	28	+5	5622·3	17781	8	28
2	5414·3	18464	8	26	4	5638·0	17732	12	31

TABLE I—(*Contd.*).

Int.	λ-in air	ν-in vac.	v'	v''	Int.	λ-in air	ν-in vac.	v'	v''
3	5420·2	18444	5	24	+ *d*3	5653·1	17685	9	29
*d*2	5426·5	18423	12	29	+ *d*3	5667·9	17638	6	27
*d*1	5445·2	18360	9	27	*d*2	5674·1	17619	13	32
3	5452·4	18335	6	25	+ *d*2	5683·9	17589	10	30
+2	5458·2	18316	3	23	+ 2	5698·0	17545	7	28
1	5464·5	18295	13	30	3	5714·1	17496	11	31
+5	5471·4	18272	10	28	4	5719·3	17480	4	26
+2	5485·1	18226	7	26	4	5730·8	17445	8	29
3	5488·7	18214	4	24	+ 3	5745·7	17400	12	32
3	5496·7	18188	14	31	+ 3	5761·5	17352	9	30
+5	5502·4	18169	11	29	+ 5	5779·6	17297	13	33
4	5518·5	18116	8	27	+ 3	5792·8	17258	10	31
+*d*1	5533·1	18068	12	30	+ 0	5808·9	17210	7	29
+*d*1	5547·6	18021	9	28	+ 0	5825·4	17161	11	32
+*db*2	5559·6	17982	6	26	1	5833·3	17138	4	27
+ *d*4	5576·0	17929	10	29	+ 1	5839·1	17121	8	30
+ 4	5591·3	17880	7	27	3	5858·0	17063	5	28
+ 4	5606·8	17831	11	30	+ 2	5873·0	17022	9	31

d = diffuse bands, *db* = diffuse and broad bands.

+, these bands form according to Nevin, the green yellow system which is the same as system of fluctuation No. 6, Fig. 2.

TABLE II.

(Table showing the vibrational differences for the initial state according to Nevin's measurements and analysis.)

v' \ v''	0	1	2	3	4	5	6	7	8	9	Mean
5–6					246·0	248·0	248·0				247·6
6–7		263·0			252·0	248·0	251·0	249·0	250·0		252·2
7–8	239·9	234·0			238·0	234·0	232·0	237·0	237·0	232·0	235·5
8–9	227·6	231·0	228·0	233·0	230·0	236·0	234·0	234·0	233·0	240·0	232·7
9–10	235·5	222·2	227·4	223·0	229·0	235·0	235·0	235·0	227·0	209·0	227·8
10–11	204·5	209·9		212·0							208·0
11–12	218·9			206·0							213·4
12–13	212·6		214·5	225·5							217·5
13–14	212·8	216·6	213·5	211·0							213·2
14–15	207·8										207·8
15–16	203·3										202·3
16–17	201·3										201·3
17–18	197·1										197·1
18–19	195·7										195·7
19–20	184·6										184·6
20–21	173·8										173·8
21–22	156·6										156·6

TABLE III.

(Table showing the vibrational differences for the final state according to Nevin's measurements and analysis.)

v' \ v''	0–1	1–2	2–3	3–4	4–5	5–6	6–7	7–8	8–9	9–10
5					385·0	381·0				
6		380·0			383·0	383·0	381·0	380·0		
7	371·0				387·0	378·0	383·0	379·0	371·0	
8	376·9	382·0	385·0	383·0	391·0	380·0	378·0	379·0	376·0	
9	373·5	385·0	380·0	386·0	385·0	382·0	378·0	380·0	369·0	
10	386·8	379·8	384·4	380·0	379·0	382·0	378·0	388·0	387·0	378·0
11	387·4									
12			391·0							
13	380·6	381·9	380·0	377·5						
14	376·8	385·0	382·5							
Mean	378·1	382·4	383·8	381·6	385·0	381·0	379·6	381·2	375·6	378·0

TABLE IV.

Unclassified bands.

Int.	λ-in air	ν-in vac.	Int.	λ-in air	ν-in vac.
*d*2	4415·8	22640	*d*1	4726·5	21151
*d*1	4482·3	22304	*d*1	4765·1	20980
*d*1	4486·2	22284	2	4782·5	20904
*d*2	4530·9	22065	*d*1	4783·6	20899
1	4583·2	21813	*d*1	4786·5	20886
*d*2	4604·9	21710	1	4792·7	20859
*d*1	4647·2	21512	*d*1	4812·2	20775
*d*2	4683·9	21344	*d*1	4842·6	20644
			*d*1	4866·7	20542

d = diffuse.

v' \ v''	0	1	2	3	4	5	6	7	8	9	10	11	12
0										22525	22155		21417
1										22778	22411	22045	21686
2											22692	22323	21942
3												22596	
4									23982		23214		22488
5											23495		22739
6							25247	24870	24486	24096			
7							25495	25114	24735	24360			23233
8						26115	25727	25351	24975	24597			23479
9							25967	25587			24453		23707
10							26201	25819			24691		
11											24901		
12												24789	24422
13													
14													
15													
16													

TABLE V.

12	13	14	15	16	17	18	19	20	21	22	23	24	25
21417	21046	20670	20298	19924	19554	19206							
21686	21319	20932		20202	19828	19471	19130	18786					
21942	21591	21211		20470					18727				
	21849	21484		20743	20394			19365	18999	18656	18316		
22488	22130		21391	21029		20325	19979		19245		18554	18214	
22739	22380						20222	19848	19484		18798	18444	
	22617			21537	21184	20812	20464	20111		19390	19040	18685	18335
23233		22507		21772		21059	20709	20352			19284	18931	18578
23479		22755			21658			20582		19866	19510	19170	18830
23707						21548					19758	19409	19060
						21798					20000		19299
											20239	19883	19547
24422			23302							20852		20133	19788
												20359	20022
											20954		
													20500

	25	26	27	28	29	30	31	32	33
4		17480	17138						
4				17063					
5	18335	17982	17638						
1	18578	18226	17880	17545	17210				
0	18830	18464	18116	17781	17445	17121			
9	19060	18712	18360	18021	17685	17352	17022		
	19299			18272	17929	17589	17258		
3	19547	19188	18850	18510	18169	17839	17496	17161	
3	19788	19434	19082	18748	18423	18068	17732	17400	
9	20022			18965		18295		17619	17297
		19901			18889	18536	18188		
	20500			19446	19101	18757			
					19324	18982			

TABLE VI.

(Table showing vibrational differences for the initial state according to the analysis proposed in this paper.)

v'' / v'	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	Mean
0—1				253	256		269	273	262		278	274	265															267·5
1—2					281	278	256	272	279		268																	272·3
2—3						273		258	273		273					272												270·0
3—4								281			286					246		238										262·7
4—5					281		251	250						243		239		244	230									256·3
5—6														242	263			242	241									247·0
6—7	248	244	249	264							235		247	245	241			244	246	243	244	242						245·5
7—8	232	237	240	237			246		248						230			226	239	252	238	236	236	235				238·0
8—9	240	236					228											248	239	230	248	244	240	240	231			238·5
9–10	234	232			238								250					242		239			251	244	237	236		240·0
10–11					210													239		248			238	240	242	238		235·0
11–12																			250	241	246	232	238	254	237	264	239	244·5
12–13																			226	234			217		227		219	224·6
13–14																									241			241·0
14–15																								212	221			216·5
15–16																								223	225			224·0

TABLE VII.

(Table showing the vibrational differences for the final state accor

v' / v''	5–6	6–7	7–8	8–9	9–10	10–11	11–12	12–13	13–14	14–15	15–16	16–17	17–18	18–19	19–20	20–2
0					370			371	376	372	374	370	348			
1					367	366	359	367	387			374	357	341	344	
2						369	381	351	380							
3									365			349				366
4								358			362			346		
5								359							374	364
6		377	384	390								353	372	348	353	
7		381	379	375										350	357	
8	388	376	376	378												
9		380														
10		382														
11																
12																
13																
14																
15																
16																
Mean	388·0	379·2	379·7	381·0	368·5	367·5	370·0	359·0	377·0	372·0	368·0	361·5	359·0	346·3	357·0	365

I.

te according to the analysis proposed in this paper.)

–20	20–21	21–22	22–23	23–24	24–25	25–26	26–27	27–28	28–29	29–30	30–31	31–32	32–33
344													
	366	343	340										
				340			342						
374	364			354									
353			350	355	350	353	344						
357				353	353	352	346	335	335				
			356	340	340	366	348	335	336	324			
				349	349	348	352	339	336	333	330		
									343	340	331		
				356	336	359	338	340	341	338	335	335	
					345	354	352	334	325	355	336	332	
					337								322
										353	348		
										344			
										342			
357·0	365·0	343·0	348·5	349·6	344·3	355·3	346·0	336·6	336·0	341·1	336·0	333·5	322·0

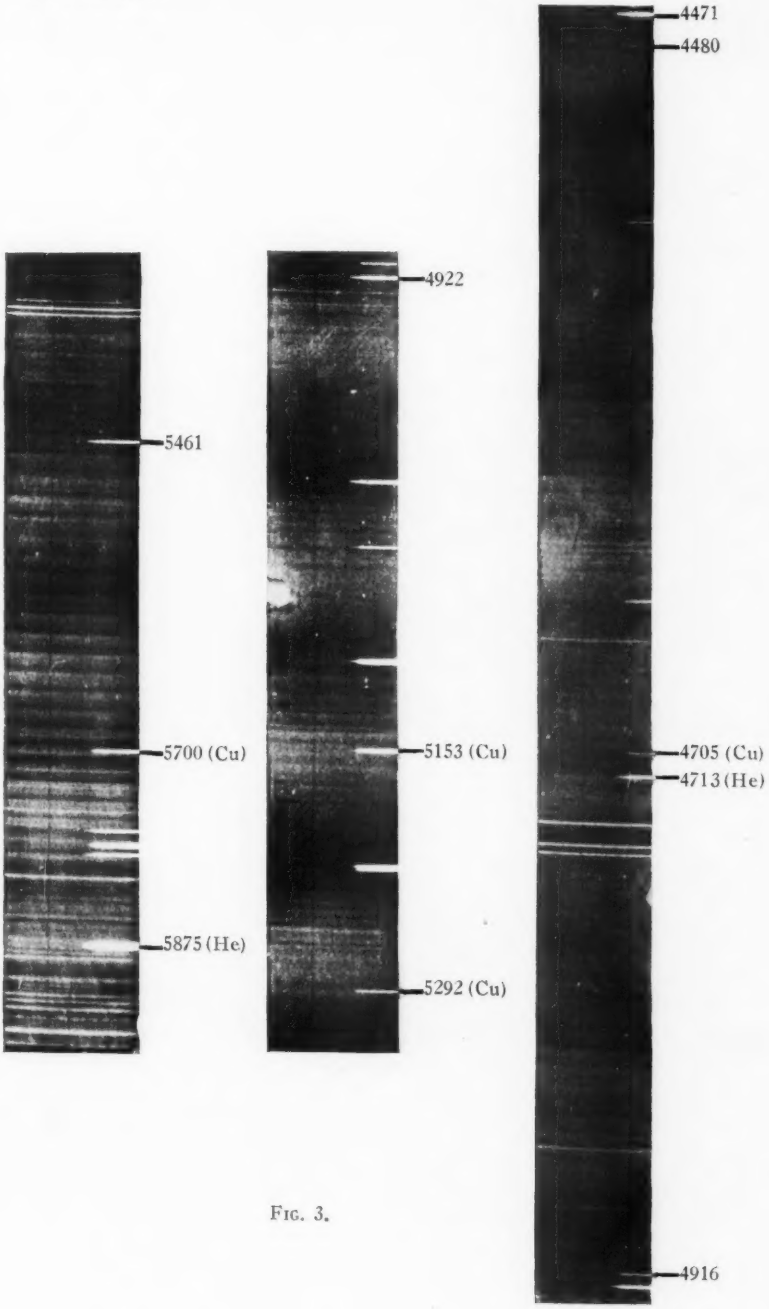
4471
4480
4922
5461
5700 (Cu)
5153 (Cu)
4705 (Cu)
4713 (He)
5875 (He)
5292 (Cu)
4916

FIG. 3.

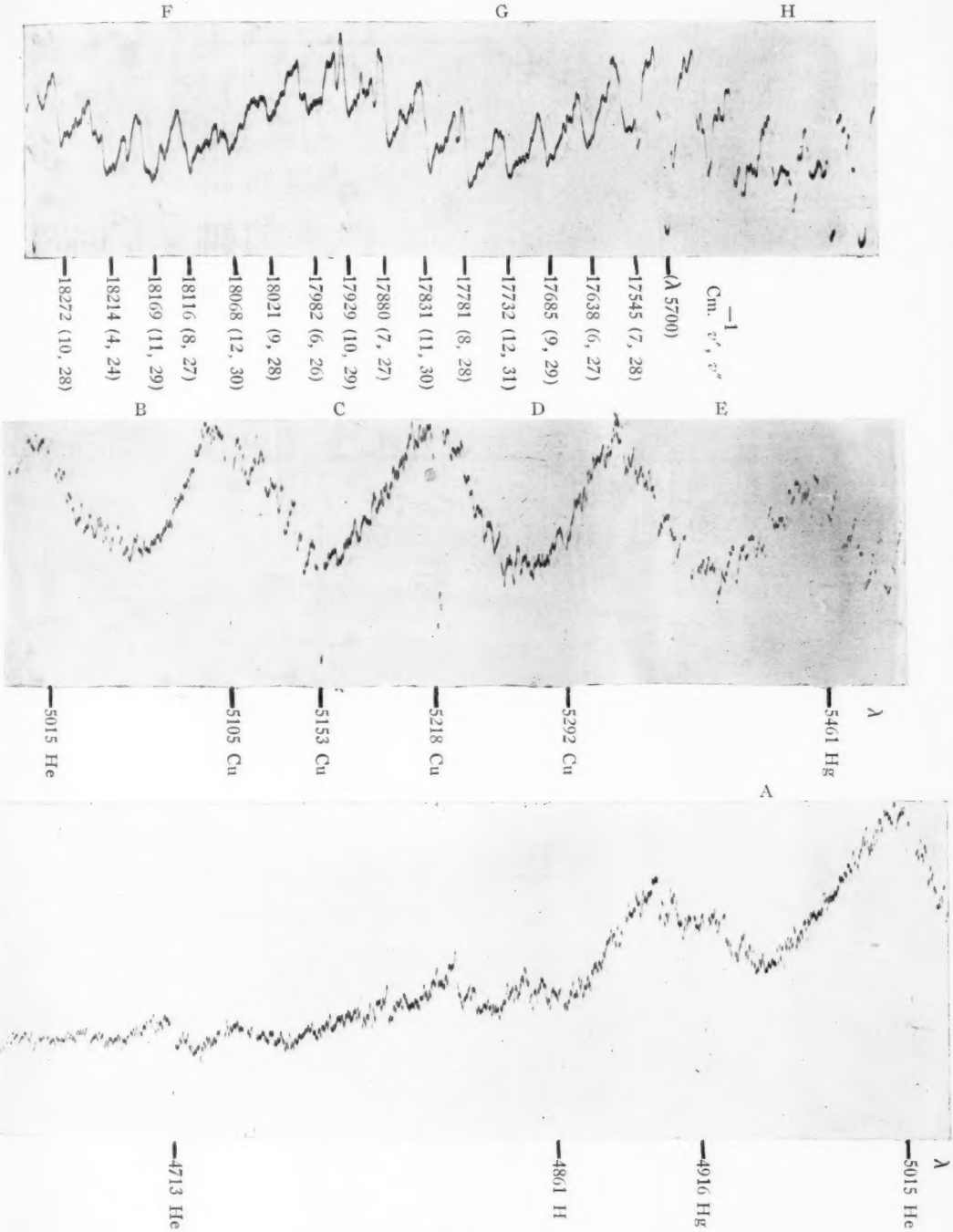
F
G
H
18272 (10, 28)
18214 (4, 24)
18169 (11, 29)
18116 (8, 27)
18068 (12, 30)
18021 (9, 28)
17982 (6, 26)
17929 (10, 29)
17880 (7, 27)
17831 (11, 30)
17781 (8, 28)
17732 (12, 31)
17685 (9, 29)
17638 (6, 27)
17545 (7, 28)
(λ 5700)
Cm.
B
C
D
E
5015 He
5105 Cu
5153 Cu
5218 Cu
5292 Cu
5461 Hg
λ
A
4713 He
4861 H
4916 Hg
5015 He
λ

FIG. 4.

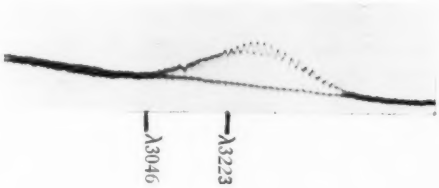

FIG. 9.

NUCLEAR SPIN OF RHODIUM.

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Rhodium, according to Aston,[1] consists of a single isotope of mass 103. Fermi[2] has observed the presence of two periods of artificial radio-active decay for this element ; on irradiation with slow neutrons, rhodium emits β-rays of two periods with half-lives 44 secs., and 3·9 mins. Suspecting that the double period might arise from an undiscovered additional isotope, Sampson and Bleakney[3] have recently submitted the element to a mass spectrographic study with a new ion source. They have thus established the existence of Rh 101 present to one part in 1300 of Rh 103. In study of the hyperfine structure of rhodium lines, however, the rôle of Rh 103 only need be considered as the other isotope Rh 101 has relatively a negligibly small abundance. The object of the present investigation is to determine from hyperfine structure data of the arc lines of rhodium the nuclear spin of Rh 103. White[4] has given it as 5/2 ; this result has presumably arisen from a possible confusion between rhenium and rhodium, which exists in Gibbs' Bibliography of Line Spectra of the Elements.[5] The hyperfine structure of the rhodium lines has therefore been investigated here with the conclusion that the isotope Rh 103 has a nuclear spin of $\frac{1}{2}$ with a small positive magnetic moment.

The rhodium arc lines were obtained from a water-cooled hollow cathode source previously described.[6] The lines involving the deepest levels $4d^8\ 5s\ {}^4F_{4\frac{1}{2},\ 3\frac{1}{2}}$ were examined for structure with a quartz Lummer-Gehrcke plate 3·45 mm. thick and 20 cm. long. The following arc lines with the common level ${}^4F_{3\frac{1}{2}}$ were observed to be single :

---

[1] Aston, *Proc. Roy. Soc.*, 1935, **149**, 397.

[2] Fermi, *ibid.*, 1934, **146**, 483.

[3] Sampson and Bleakney, *Phys. Rev.*, 1936, **50**, 732.

[4] White, *Introduction to Atomic Spectra*, 1934, p. 372.

[5] Gibbs, *Rev. Mod. Phys.*, 1932, **4**, 399.

[6] For experimental details *vide* Venkatesachar and Sibaiya, *Proc. Ind. Acad. Sci.*, 1935, **1**, 955.

λ in Å	Classification[7]
3528·0 ..	$4d^8\ 5s\ {}^4F_{3\frac{1}{2}} - 4d^8\ 5p\ {}^4F^0_{3\frac{1}{2}}$
3583·1 ..	$4d^8\ 5s\ {}^4F_{3\frac{1}{2}} - 4d^8\ 5p\ {}^4F^0_{4\frac{1}{2}}$
3658·0 ..	$4d^8\ 5s\ {}^4F_{3\frac{1}{2}} - 4d^8\ 5p\ {}^4D^0_{2\frac{1}{2}}$
3701·2 ..	$4d^8\ 5s\ {}^4F_{3\frac{1}{2}} - 4d^8\ 5p\ {}^4G^0_{4\frac{1}{2}}$

Two arc lines having a common level in the ground term $^4F_{4\frac{1}{2}}$ show a doublet structure :

λ in Å	Classification[7]	Structure in cm.$^{-1}$
3434·9 ..	$4d^8\ 5s\ {}^4F_{4\frac{1}{2}} - 4d^8\ 5p\ {}^4G^0_{5\frac{1}{2}}$	0·000(11), + 0·058(9)
3692·4 .	$4d^8\ 5s\ {}^4F_{4\frac{1}{2}} - 4d^8\ 5p\ {}^4D^0_{3\frac{1}{2}}$	0·000(11), + 0·058(9)

The above doublet structure does not arise from self-reversal because the resonance lines of copper have been observed unreversed under the same conditions of discharge ; besides this the melting and boiling points of rhodium are higher than those of copper. Assuming that the upper levels are negligibly split, the observed structure of the last two lines can be explained as arising from a splitting of the ground term $^4F_{4\frac{1}{2}}$ when a nuclear spin of $\frac{1}{2}$ is ascribed to Rh 103 (*vide* Fig. 1).

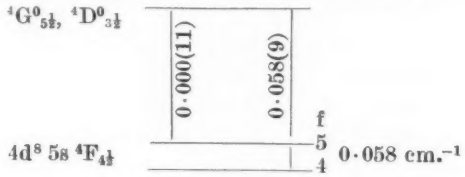

FIG. 1.

A microphotograph of λ 3434·9 Å (Fig. 2)* shows its two components with their relative intensities. The smallness of the hyperfine structure interval

[7] Meggers and Laporte, *Phys. Rev.*, 1926, **28**, 654 ; also Sommer, *Zeits. f. Physik.*, 1927, **45**, 147.

* The microphotograph was taken by me at the Indian Institute of Science with the kind permission of the Director, Sir C. V. Raman.

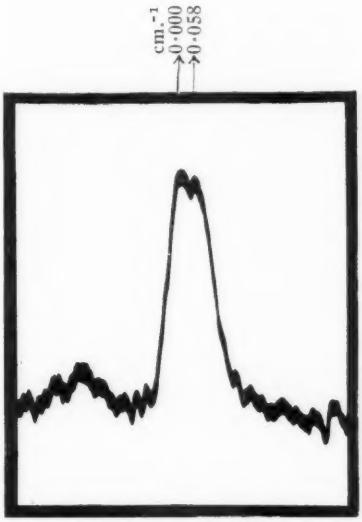

FIG. 2. Microphotograph of the Structure Pattern of RhI λ 3434·9Å.

factor of $^4F_{4\frac{1}{2}}$, *viz.*, 0·012 cm.$^{-1}$ shows that the magnetic moment of the rhodium nucleus is small ; its value is however positive because the hyperfine levels of $^4F_{4\frac{1}{2}}$ are erect. Rhodium, with an odd atomic number (45) and an odd mass number (103) belongs to the nuclear class II of Grace[8] where the magnetic moments are all positive and the g-factors vary from nearly zero to 4·2.

I wish to thank Prof. A. Venkat Rao Telang for his kind interest during the progress of this work.

[8] Norman S. Grace, *Phys. Rev.*, 1933, **44**, 362.

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